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formed with ammonium molybdate being used for this purpose. In this investigation we have employed a variant of this method, developed by one of us [5], which permits separate determination in the solution of molecularly dispersed and polymerized silicic acid. In the latter case a preliminary treatment with alkaline solutions is given. When it was found necessary, a more sensitive method of silicic acid determination was used: the method proposed by Usatenko and Orlova [6], in which the silicomolybdate complex is reduced with Mohr's salt to molybdenum blue. The amounts of alkali and silicic acid found in the solution were then recalculated as moles of the corresponding oxides (Na_2O and SiO_2) going into solution from 1 sq.cm of surface (denoted by n_{Na_2O} and n_{SiO_2}). This method of expressing the analytical results makes it easy to compare the amounts of the components going into solution with their contents in the original glass, and it facilitates the interpretation of the results obtained.

In order to characterize the process of interaction we employed also several other quantities. If the composition of the glass is expressed in the form $mNa_2O \cdot nSiO_2$, then the amount of SiO_2 in the layer of glass that has undergone reaction will be $m \cdot n_{Na_2O}$ and the fraction of this (α) which has passed from this layer to the solution will be $\frac{n_{SiO_2}}{m \cdot n_{Na_2O}}$. Thus α is the fraction of the silicic acid that has passed into the solution from the layer of glass that has undergone reaction, and its value permits us to form an idea of the nature of the process that is taking place. When $\alpha = 1$, the components are passing into the solution in the same proportions as those in which they occur in the glass, i.e. dissolution is occurring. On the other hand, when $\alpha = 0$, leaching is occurring, with the result that a layer of silicic acid remains on the surface of the glass. Furthermore, knowing the amount of Na_2O that has passed into solution, we may, with certain assumptions, calculate the depth of the disrupted layer of glass, the required formula being:

$$\delta_{Na_2O} = \frac{n_{Na_2O} \cdot M \cdot 100}{ad}, \qquad (2)$$

TABLE 2

Interaction of Vitreous Sodium Silicates with Water at 25°

Molar ratio $Na_2O:SiO_2$	Coefficients	Time										
		minutes					hours					
		2.5	5	10	15	30	1	2	4	6	8	12
1:1	$n_{Na_2O} \cdot 10^6$	246	590	1250	—•	—••	8000•••	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	245	590	1260	—	—	8000•••	—	—	—	—	—
	α	1.00	1.00	1.01	—	—	1.0	—	—	—	—	—
1:1.4	$n_{Na_2O} \cdot 10^6$	4.1	7.5	13	19	35	79	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	2.6	4.4	8.8	14	35	101	—	—	—	—	—
	α	0.45	0.42	0.46	0.53	0.71	0.91	—	—	—	—	—
1:1.7	$n_{Na_2O} \cdot 10^6$				6.0	10	17	28	45	61	—	—
	$n_{SiO_2} \cdot 10^6$				1.8	2.2	3.4	5.3	12	18	—	—
	α				0.18	0.13	0.12	0.11	0.16	0.17	—	—
1:2	$n_{Na_2O} \cdot 10^6$					4.6	7.6	13	20	26	32	45
	$n_{SiO_2} \cdot 10^6$					0.2	0.6	1.2	2.1	2.6	3.0	3.5
	α					0.02	0.04	0.05	0.05	0.05	0.05	0.04

• It was now no longer possible to take the surface area as having its initial value.
•• The sample dissolved completely.
••• Extrapolation.

where n_{Na_2O} is the amount of Na_2O going into the solution (moles/sq.cm); M is the molecular weight of Na_2O; a is the amount of Na_2O in the glass (wt. %); d is the density of the glass.

The value of δ_{SiO_2}, expressing the reduction in the thickness of the silicic acid layer due to its dissolution, may be calculated in a similar manner. The difference in these quantities, $\delta = \delta_{Na_2O} - \delta_{SiO_2}$, gives the thickness of the silicic acid layer on the surface of the glass. This calculation, of course, is of a conditional nature, for it is

TABLE 3

Interaction of Vitreous Sodium Silicates with Water at 40°

Molar ratio $\frac{Na_2O}{SiO_2}$	Coefficients	Time: Minutes 2.5	5	7.5	10	15	30	Hours 1	2	4	6	8	12
1/1	$n_{Na_2O} \cdot 10^6$	458	1030	1470	—•	—	—••	12000•••	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	450	1040	1500	—	—	—	12000•••	—	—	—	—	—
	α	1.0	1.0	1.0	—	—	—	1.0	—	—	—	—	—
1/2.4	$n_{Na_2O} \cdot 10^6$	15	34	—	72	108	218	439	—	—	—	—	—
	$n_{SiO_2} \cdot 10^6$	18	46	—	100	152	304	605	—	—	—	—	—
	α	0.86	0.97	—	0.99	1.00	1.00	1.0	—	—	—	—	—
1/3.7	$n_{Na_2O} \cdot 10^6$	3.6	6.4	—	8.2	14	28	51	104	220	342	—	—
	$n_{SiO_2} \cdot 10^6$	1.6	2.8	—	4.6	7.2	15	33	140	350	566	—	—
	α	0.26	0.26	—	0.33	0.30	0.31	0.38	0.79	0.94	0.97	—	—
1/2	$n_{Na_2O} \cdot 10^6$	1.7	2.8	—	4.9	6.6	11	18	30	47	62	76	101
	$n_{SiO_2} \cdot 10^6$	0.07	0.25	—	0.66	1.2	2.3	3.2	4.2	5.8	9.3	13	26
	α	0.02	0.04	—	0.07	0.09	0.10	0.09	0.07	0.06	0.08	0.09	0.13
1/2.3	$n_{Na_2O} \cdot 10^6$						5.1	9.1	15	25	32	38	51
	$n_{SiO_2} \cdot 10^6$						0.12	0.24	0.54	0.83	1.0	1.3	2.1
	α						0.010	0.011	0.014	0.015	0.014	0.015	0.018
1/3	$n_{Na_2O} \cdot 10^6$							1.6	2.5	3.6	4.7	5.5	7.2
	$n_{SiO_2} \cdot 10^6$							0.040	0.046	0.065	0.078	0.092	0.11
	α							0.008	0.006	0.006	0.006	0.006	0.005
1/4	$n_{Na_2O} \cdot 10^6$							0.75	0.93	1.2	1.4	1.6	2.0
	$n_{SiO_2} \cdot 10^6$							0.016	0.017	0.022	0.030	0.038	0.040
	α							0.005	0.005	0.005	0.005	0.006	0.005
1/6	$n_{Na_2O} \cdot 10^6$							0.30	0.38	0.48	0.55	0.61	0.69
	$n_{SiO_2} \cdot 10^6$							0.009	—	0.012	0.011	0.012	0.013
	α							0.005	—	0.004	0.003	0.003	0.003

• It was now no longer possible to take the surface area as having its initial value.

•• The sample dissolved completely.

••• Extrapolation.

made on the supposition that the residual film consists only of silicic acid and does not contain Na_2O, and that the boundaries between unchanged glass and film and between film and solution are parallel to the original surface of the glass the dissolution of silicic acid occurring only from the surface of the film. Also, this calculation takes no account of the change in the volume of the film, as compared with the volume of the original glass. Nevertheless, in spite of the conditional nature of the calculations, the results obtained permit a very graphic comparison of the various sodium silicates. Thus, by the aid of the method described above it has been possible to characterize the course of the breakdown process in sodium silicates.

Interaction of Sodium Silicates with Water

The experiments were carried out on eight sodium silicates. The results relating to the interaction of these silicates with water at 25°, 40°, and 100° are given in Tables 2, 3, and 4, and also in Fig. 2. The duration of the experiment varied from ten minutes to twelve hours, depending on the composition of the silicate.

TABLE 4

Interaction of Vitreous Sodium Silicates with Water*

Coefficients	$Na_2O : SiO_2$				
	1:2	1:2.3	1:3	1:4	1:6
$\frac{n_{Na_2O}}{m} \cdot 10^6$	3200	990	69	5.8	1.4
$\frac{n_{SiO_2}}{m} \cdot 10^6$	6400	2200	102	1.4	0.12
α	1.0	0.97	0.49	0.060	0.014

It will be seen from the results given in Tables 2 and 3 that in the case of the interaction of sodium metasilicate with water at 25° and 40° the components of the glass go into solution in the same ratio as that in which they are found in the glass; dissolution is therefore occurring (α = 1). Dissolution is very rapid: a 2-g sample dissolved completely in 15-20 minutes, yielding a clear solution.

As the silica content of the sodium silicates increases, there is a considerable reduction in the absolute amounts of the components going into solution, and the transfer of SiO_2 lags behind that of Na_2O. Consequently, the value of α diminishes, which is evidence of the presence of a residual layer of silica on the surface of the glass. For the silicate of composition $Na_2O \cdot 1.4SiO_2$, however (and to some extent also for $Na_2O \cdot 1.7SiO_2$ at 40°), an appreciable lag in the transfer of SiO_2 can be observed only in the early stages; the value of α then becomes equal to, or nearly equal to, unity. This may be explained, on the one hand, by the increase in the alkalinity of the solution with time due to the entry of Na_2O from the glass: this leads to dissolution of the surface layer of silicic acid that has formed, and so to a reduction in its thickness. On the other hand, the thinning of the silicic acid layer facilitates the passage of Na_2O into the solution, and so itself contributes to the thickening of the layer. As a result, an equilibrium is established in which the thickness of the film increases, because of the passage of Na_2O into solution, to almost the same extent as it diminishes because of dissolution of silicic acid from the surface. Dissolution of the glass appears to occur, and it proceeds in such a way that there is always a layer of silicic acid on the surface; as a result, the value of α approaches unity only asymptotically.

Experiments with sodium disilicate at 25° and 40° showed that α has values of 0.02-0.13. The silicic acid film is now stronger, and its restraining action on the transfer of Na_2O into solution is quite marked. In the case of silicates of higher silica content, only an insignificant amount of the silicic acid passes into solution at 40° (α = 0.02-0.003); the bulk of it remains on the surface. When the temperature is raised to 100°, the amounts of the components (particularly SiO_2) going into solution increase considerably (see Table 4); as a result the value of α increases, indicating in the case of the less stable silicates, e.g. $Na_2O \cdot 2SiO_2$, a transition from leaching to dissolution.

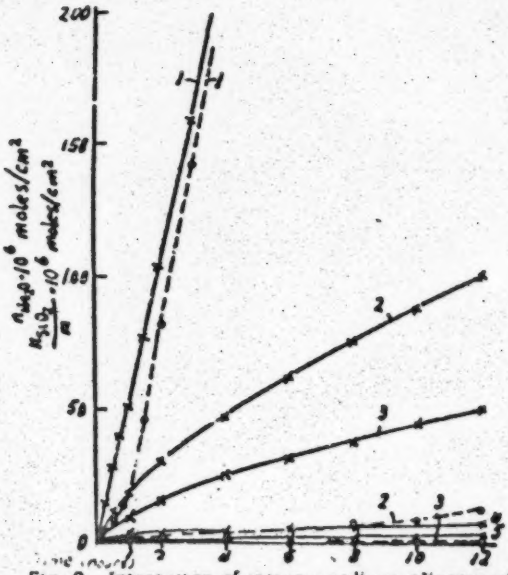

Fig. 2. Interaction of vitreous sodium silicates with water at 40°. 1 - $Na_2O \cdot 1.7\,SiO_2$; 2 - $Na_2O \cdot 2SiO_2$; 3 - $Na_2O \cdot 2.3\,SiO_2$; 4 - $Na_2O \cdot 3SiO_2$; 5 - $Na_2O \cdot 4SiO_2$; x-x-$\frac{n_{Na_2O}}{m}$ o-o-$\frac{n_{SiO_2}}{m}$

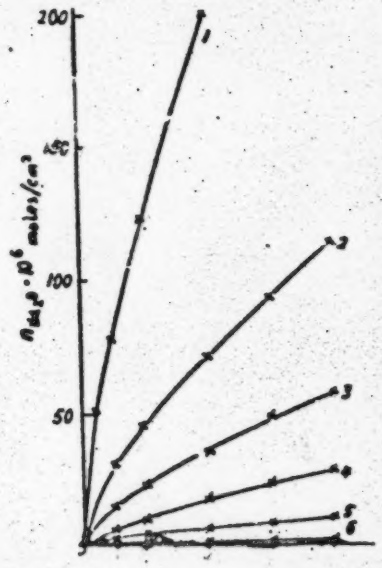

Fig. 3. Interaction of vitreous sodium silicates with 0.1 N hydrochloric acid: 1) $Na_2O \cdot 1.7\,SiO_2$; 2) $Na_2O \cdot 2SiO_2$; 3) $Na_2O \cdot 2.3\,SiO_2$; 4) $Na_2O \cdot 2.6\,SiO_2$; 5) $Na_2O \cdot 3SiO_2$; 6) $Na_2O \cdot 4SiO_2$

* Experiments were at 100° for one hour.

It was established that when sodium silicates interact with water the whole of the silicic acid going into solution is in a molecularly dispersed state and may be determined, without preparatory treatment, by the colorimetric method.

Interaction of Sodium Silicates with Hydrochloric Acid Solutions

A study was made of the interaction of six sodium silicates with 0.1 N hydrochloric acid at 40°. In order to determine the effect of the concentration of acid on the susceptibilities of sodium silicates to attack, an investigation was made of the action of 0.01 N, 0.1 N, and N solutions of hydrochloric acid on a sodium silicate of molecular composition $Na_2O \cdot 2.6SiO_2$. The experiments were of eight hours' duration, and tests were made after 1, 2, 4, 6, and 8 hours. The results on the action of acids on the investigated sodium silicates are given in Table 5 and in Fig. 3. As will be seen from these results, the extent to which Na_2O passes into the solution falls rapidly as the SiO_2 content of the original silicate increases, as in the case of the experiments with water. The absolute values of the amounts of Na_2O passing into solution are higher for the acid solutions than for water. Beginning with the silicate of composition $Na_2O \cdot 4SiO_2$, the amount of Na_2O passing into solution becomes very small (not more than $2 \cdot 10^{-6}$ moles/sq. cm in eight hours, both in the case of water and of acids). The action of acids is characterized by a more marked lag of silicic acid behind Na_2O in its passage into the solution. Even with such an unstable silicate as $Na_2O \cdot 1.7SiO_2$, an appreciable layer of silicic acid remains on the surface after a four hours' treatment with acid ($a = 0.227$), whereas for treatment with water under these conditions a approaches unity and this silicate practically dissolves.

TABLE 5

Interaction of Vitreous Sodium Silicates with Hydrochloric Acid Solutions at 40°

Molar ratio $Na_2O : SiO_2$	Normality of acid	Coefficients	Time (hours)					
			0.5	1	2	4	6	8
1:1.7	0.1	$n_{Na_2O}\ 10^6$	51.6	78.1	122.6	200.9	–	–
		$n_{SiO_2}\ 10^6$	0.3	0.7	5.4	77.8	–	–
		a	0.003	0.005	0.026	0.227	–	–
1:2.0	0.1	$n_{Na_2O}\ 10^6$		29.9	46.5	71.1	94.2	108.9
		$n_{SiO_2}\ 10^6$		0.02	0.03	0.1	0.2	0.3
		a		0.0003	0.0003	0.0007	0.001	0.001
1:2.3	0.1	$n_{Na_2O}\ 10^6$	–	14.9	22.4	35.3	48.4	57.2
		$n_{SiO_2}\ 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:2.6	0.01	$n_{Na_2O}\ 10^6$	–	5.6	9.6	16.8	22.3	26.5
		$n_{SiO_2}\ 10^6$	–		0	0	0	0
		a	–	0	0	0	0	0
1:2.6	0.1	$n_{Na_2O}\ 10^6$	–	6.0	10.2	18.5	22.8	28.2
		$n_{SiO_2}\ 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:2.6	1	$n_{Na_2O}\ 10^6$	–	4.5	8.3	16.2	20.9	25.4
		$n_{SiO_2}\ 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:3.0	0.1	$n_{Na_2O}\ 10^6$	–	2.7	4.3	5.7	8.1	10.0
		$n_{SiO_2}\ 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0
1:4.0	0.1	$n_{Na_2O}\ 10^6$	–	0.7	1.0	1.2	1.5	1.7
		$n_{SiO_2}\ 10^6$	–	0	0	0	0	0
		a	–	0	0	0	0	0

When the silicate $Na_2O \cdot 2.3SiO_2$ and silicates of higher silica content were treated with hydrochloric acid solutions, no silicic acid could be detected in the solution. On the other hand, in the water experiments silicic acid was found in the solution even in the case of the silicate $Na_2O \cdot 6SiO_2$.

As will be seen from Table 5, variation in hydrochloric acid concentration from 0.01 N to N has practically no effect on the amount of Na_2O passing into solution from the silicate of composition $Na_2O \cdot 2.6\ SiO_2$.

DISCUSSION OF RESULTS

The way in which the amounts of the components passing into solution depend on the silica contents of the sodium silicates submitted to the action of water and of hydrochloric acid solutions is shown in Figures 4 and 5. In the case of water, these figures show that the relationship is expressed by a number of similar smooth curves.

For the action of hydrochloric acid solutions at 40°, the relationship between the logarithm of the amount of Na_2O passing into solution and the molecular proportion of SiO_2 in the glass is almost a linear one (Fig. 5). Both for water and for acids there are no perceptible deviations at compositions corresponding to the invariant points of the Na_2O-SiO_2 phase diagram. It will be seen from the results presented that increase in silica content has a particularly marked effect in reducing the tendency for leaching to occur from sodium silicate glasses when the latter are based on silicates of low stability, further increase in silica content does not have such a powerful effect. Features described by other investigators who have studied the stability of sodium and potassium silicate glasses [7] – a linear logarithmic relation between the amount of alkali passing into solution and the molecular proportion of SiO_2 in the glass, and deviations at the points corresponding to disilicate – have not been confirmed in our experiments.

The interaction of vitreous sodium silicates with aqueous solutions is extremely complex and depends on a number of factors. The main factors determining the rate of the breakdown of sodium silicates are: the state of the silica in the original glass, the hydrogen ion concentration in the solution, and the thickness and structure of the protective surface film. The latter is, of course, largely determined by the state of silica in the original glass.

As will be seen from the results presented, the main process occurring in sodium silicates having a relatively high silica content (and therefore a relatively high number of directly united silicon-oxygen tetrahedra) is the leaching out of sodium oxide by water. The alkaline solution formed as a result of the exchange of sodium ions for hydrogen ions is not able to disrupt the robust skeleton to an appreciable extent: evidence for this is to be found in the low concentration of SiO_2 in the solution.

In the case of silicates such as $Na_2O \cdot 1.4\,SiO_2$, $Na_2O \cdot 1.7\,SiO_2$, and (at higher temperatures) $Na_2O \cdot 2SiO_2$, which have relatively weakly polymerized skeletons, formation of alkali in the solution leads to transfer also of SiO_2 from the protective surface layer in a molecularly dispersed form, and what may be regarded as dissolution of the glass occurs.

Change in temperature has a considerable influence on this secondary process: dissolution of silicic acid from the surface. Fig. 6 shows the variation with composition and temperature of the proportion α of silicic acid passing into solution when vitreous sodium silicates are treated with water for one hour. As will be seen from Figures 4 and 6, as the temperature rises the amounts of the components passing into solution increase considerably, and at the same time the boundary of the region of soluble silicates moves in the direction of higher silica content in the original glass.

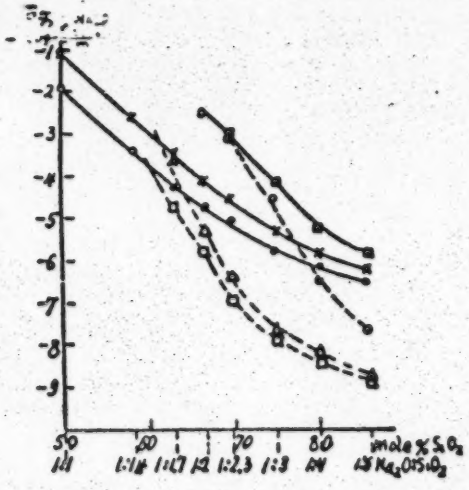

Fig. 4. Effect of composition on the amounts of the components going into solution when water acts on vitreous sodium silicates: —●— $\log n_{Na_2O}$, 40°, 1 hour; —×— $\log n_{Na_2O}$, 40°, 6 hours; —■— $\log n_{Na_2O}$, 100°, 1 hour; —□— $\log \frac{n_{SiO_2}}{m}$, 40°, 1 hour; —Δ— $\log \frac{n_{SiO_2}}{m}$, 40°, 6 hours; —○— $\log \frac{n_{SiO_2}}{m}$, 100°, 1 hour.

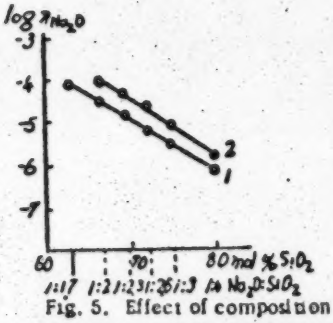

Fig. 5. Effect of composition on the amount of Na_2O going into solution when 0.1 N hydrochloric acid acts on sodium silicates: 1 – 1 hour; 2 – 6 hours.

The effect of hydrogen ion concentration on the transfer (resulting from the exchange) of sodium ions from the glass will be seen from a comparison of our results on leaching with water and with acid solutions. In the latter case a considerably greater amount of Na_2O passes into solution from the surface of the silicates investigated, and this is to be related to the marked rise in hydrogen ion

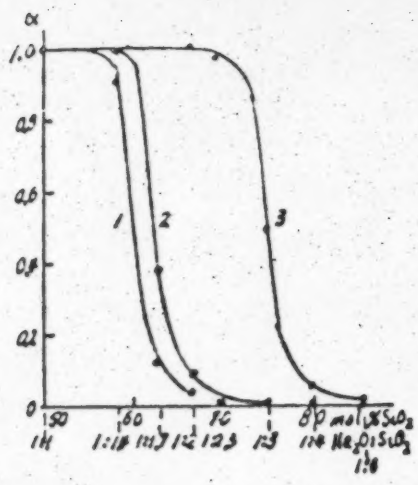

Fig. 6. Effect of composition and temperature on the proportion α of silicic acid going into solution in one hour when water acts on vitreous sodium silicates: 1) 25°, 2) 40°, 3) 100°

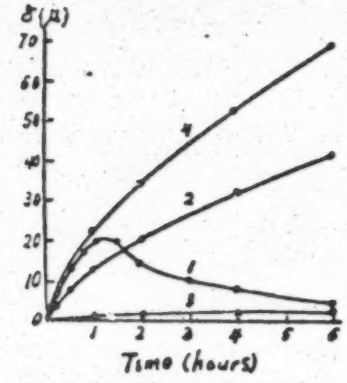

Fig. 7. Effect of the duration of treatment at 40° on the thickness of the residual layer of silicic acid on certain sodium silicates: 1) $Na_2O \cdot 1.7 SiO_2$ in water; 2) $Na_2O \cdot 2SiO_2$ in water; 3) $Na_2O \cdot 4SiO_2$ in water; 4) $Na_2O \cdot 2SiO_2$ in 0.1 N HCl.

concentration on passing from water to the acid solutions. Change in the concentration of the attacking acid in the range 0.01 N to 1 N does not correspond to such a marked change in hydrogen ion concentration, and for this reason no significant difference in the leaching of the silicate $Na_2O \cdot 2.6 SiO_2$ treated with these acids is to be observed. As indicated above, the action of the acid solutions on the silicates under investigation is accompanied by leaching. The alkali that passes into solution has little effect on the hydrogen ion concentration, because of the large excess of acid used. Solutions in which the hydrogen ion concentration is high encourage the polymerization of silicic acid and have a feeble effect on the protective surface layer; in the case of the acid treatments, therefore, no silicic acid is to be detected in the solution, even for silicates having particularly high silica contents.

The residual silicic acid layer on the surface of sodium silicates changes in thickness with time in an extremely varied manner, depending on the initial composition and on the nature of the attacking reagent. This is illustrated by the curves in Fig. 7, which are calculated from the results given in Tables 4 and 5 from the formula given above.

In the case of $Na_2O \cdot 1.7 SiO_2$, the thickness of the residual layer increases rapidly at first, but later begins to diminish as a result of dissolution of silicic acid. In this case, therefore, the silicic acid film is unstable and is unable to protect the silicate from the action of the solution. This curve clearly shows also that the primary process is the passage of Na_2O into solution (more exactly, exchange of sodium ions of the glass for hydrogen ions of the solution). The dissolution of the residual film of silicic acid is mainly determined, however, by the alkalinity of the solution, and it lags appreciably in time behind the process of film formation, which is evidence of the secondary character of this process.

In experiments with sodium disilicate at 40°, continuous increase in film thickness is observed. Even this film, however, is evidently insufficiently compact, and the amount of Na_2O passing into solution is still comparatively high. With increase in the silica content of the glass the thickness of the residual silicic acid film diminishes, and its relative growth during the course of the experiment becomes less, as will be seen by considering the example of the glass $Na_2O \cdot 4SiO_2$. Since the action of aqueous solutions on sodium silicates of high silica content consists essentially in the leaching of Na_2O from the surface, the thickness of the residual silicic acid layer is in these cases practically equal to the thickness of the layer of glass that has participated in the interaction.

The residual silica layer on sodium silicate surfaces is thicker in the case of acid attack than in the case of attack by water. The protective action of this layer, however, depends not only on its thickness, but also on its structure, which is probably determined by the state of the silica in the original silicate. Increase in the silica content of sodium silicates evidently results in the strengthening of the sodium–oxygen linkages, i.e. in a reduction of the activity of the sodium ions in the glass, which reduces their tendency to pass from the glass to the solution.

SUMMARY

1. A study has been made of the action of water and hydrochloric acid solutions on vitreous sodium silicates having compositions corresponding to the invariant points on the phase diagram of the system Na_2O–SiO_2, to intermediate points, and also to points representing high silica contents.

2. The process of interaction of sodium silicates with water can be broken down into two stages: exchange of sodium ions of the glass for hydrogen ions of the solution, resulting in the formation of a residual layer of silicic acid, which together with the silica of the original glass comprises a protective film on the surface, and reaction of the protective layer with the alkaline solution that has been formed, resulting in removal of silicic acid from the surface by dissolution.

3. In the case of sodium silicates having a low silica content, a kinetic equilibrium is established between the primary and secondary reactions, so that dissolution of the glass appears to take place. In the case of sodium silicates of high silica content, the main process is the leaching of Na_2O from the glass.

4. When sodium silicates are treated with hydrochloric acid solutions, transfer to the solution of SiO_2 lags behind that of Na_2O to a greater extent than in the case of water treatments. In the case of glasses having a silica content greater than that of disilicate, no SiO_2 could be detected in the solution.

5. The relation between the logarithms of the amounts of components passing into solution and the molecular percentage of silica in the glass is represented over the range of compositions examined by smooth curves or (in the case of acid treatment) by straight lines, without appreciable deviations at compositions corresponding to invariant points on the phase diagram of $Na_2O—SiO_2$.

6. With rise in temperature the amounts of the components passing into solution increase considerably, and at the same time the boundary of the region of soluble silicates moves in the direction of glasses of higher original silica content.

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STATE OF SILICIC ACID IN SOLUTION, AND METHODS FOR ITS COLORIMETRIC DETERMINATION

M. M. Piryutko and Yu. A. Shmidt

The colorimetric determination of silicon based on the formation of a yellow silicomolybdate complex $H_8[Si(Mo_2O_7)_6]$ has recently come into wide use [1, 2]. Nevertheless, in spite of the large number of investigations devoted to the method of determining silicic acid, the question of the effect of the form in which the silicic acid is present in the solution on the results of the colorimetric determination has as yet received inadequate study.

Silicic acid may exist in solution both as comparatively simple ions or molecules and as more complex polymeric particles that are colloidally dispersed. According to the conditions, the equilibrium between these forms may be displaced in one or the other direction. There are indications in the literature that the colorimetric determination of silicic acid with ammonium molybdate is possible only in the first case: colloidal silicic acid cannot be completely determined by the use of the usual procedure. Although this circumstance may be highly significant in the colorimetric determination of silicic acid, it is not always taken into account.

The present work was undertaken in conjunction with other investigations that are proceeding at the Institute, which demand a method for the determination of small amounts of silicic acid in solutions of various composition and varying degrees of acidity. In order to solve this problem, we considered that it was necessary to study the conditions under which silicic acid passes into the "colorimetrically undeterminable" form and to verify the methods described in the literature for determining the total amount of silicic acid present in the solution, irrespective of its condition.

EXPERIMENTAL

For the determination of the silicic acid content of a solution we employed the following procedure. A definite volume of the solution to be tested was introduced into a 25 ml measuring flask and acidified with the amount of 2 N hydrochloric acid required to give a final concentration of about 0.1 N; 5% ammonium molybdate solution (1 ml) was added, the solution was made up to volume, and, after twenty minutes was examined colorimetrically on an FEK-M photoelectric colorimeter. The method gives results accurate within $\pm 2\%$.

Experiments designed to elucidate the effect of the degree of polymerization of the silicic acid on the results of the colorimetric determination were carried out as follows. Definite volumes of a standard sodium silicate solution prepared by dissolving the soda melt of a weighed amount of silica in water were acidified with definite amounts of hydrochloric acid. In this way, solutions having definite contents of silicic and hydrochloric acids were obtained. We expressed the concentration of silicic acid in terms of SiO_2 (g/ml), and it varied from 10^{-4} to 10^{-4} g/ml SiO_2. The concentration of hydrochloric acid varied over the range 0.1 N to 5 N. The solutions were kept in paraffined flasks, and samples were taken at definite intervals and were diluted to give solutions of concentration suitable for colorimetric examination.

Experiment showed that for SiO_2 concentrations of 10^{-4} g/ml and less, no conversion of silicic acid into the "colorimetrical', undeterminable" form took place, irrespective of the acidity of the solution; i.e. no polymerization of the silicic acid occurred. At higher silicic acid concentrations, the amount actually found in the solution was usually less than the true amount. In the case of solutions containing $3\text{-}5 \cdot 10^{-4}$ g/ml SiO_2 and having a low hydrochloric acid concentration (0.1-0.2 N), there was a gradual diminution in the amount of silicic acid found in the solution by the colorimetric method. When the hydrochloric acid concentration was raised to 0.5 N and greater, the rate of conversion of silicic acid into the colorimetrically undeterminable form increased: there was a considerable fall in the amounts of silicic acid found during the first few days, and then these amounts remained practically constant for each value of the acidity (Fig. 1).

Experiments with concentrations of $10^{-3} - 10^{-3}$ g/ml SiO_2 showed that increase in silicic acid concentration led to an increased rate of conversion into the colorimetrically undeterminable form; this conversion occurs even at low acidity. In Fig. 2, curves are given that are characteristic of this range of silicic acid concentrations.

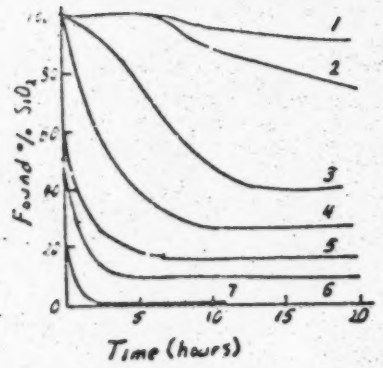

Fig. 1. Amount of silicic acid found colorimetrically in acid solutions expressed as a percentage of the true concentration ($5 \cdot 10^{-4}$ g/ml SiO_2). Concentration of hydrochloric acid: 1) 0.1 N; 2) 0.2 N; 3) 0.5 N; 4) 1 N; 5) 2 N; 6) 3 N; 7) 5 N.

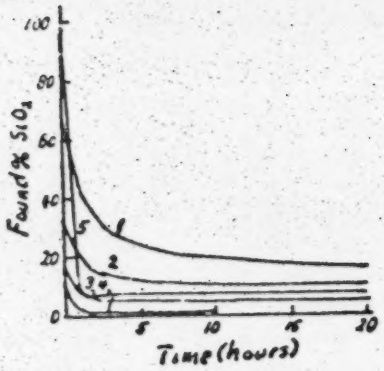

Fig. 2. Amount of silicic acid found colorimetrically in acid solutions expressed as a percentage of the true concentration ($2 \cdot 10^{-3}$ g/ml SiO_2). Concentration of hydrochloric acid: 1) 0.1 N; 2) 0.5 N; 3) 2 N; 4) 5 N; 5) neutral solution.

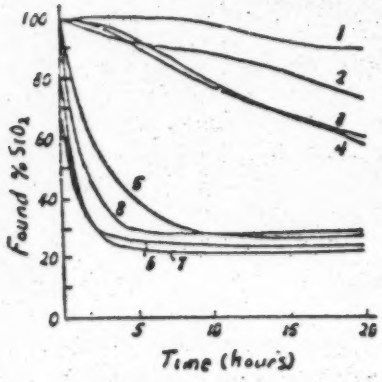

Fig. 3. Effect of salts on the amount of silicic acid found by colorimetric determination in acid solutions (true concentration, $5 \cdot 10^{-4}$ g/ml SiO_2): 1) 0.2 N HCl; 2) 0.1 N HCl + $3.8 \cdot 10^{-2}$ g/ml $AlCl_3$; 3) 0.1 N HCl + $4 \cdot 10^{-2}$ g/ml $CaCl_2$; 4) 0.1 N HCl + $4 \cdot 10^{-2}$ g/ml NaCl; 5) 1 N HCl; 6) 1 N HCl + + 3.8 10^{-2} g/ml $AlCl_3$; 7) 1 NHCl + 4 10^{-2} g/ml $CaCl_2$; 8) 1 N HCl + + 4 10^{-2} g/ml NaCl.

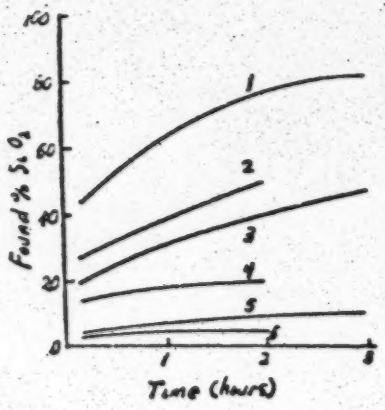

Fig. 4. Increase in intensity of color with time after addition of reagents (true concentration, $2 \cdot 10^{-3}$ g/ml SiO_2): 1) 0.1 N HCl after one day; 2) 0.1 N HCl after four days; 3) 0.5 N HCl after one day; 4) 0.5 N HCl after four days; 5) 3 N HCl after one day; 6) 3 N HCl after four days.

Experiments with a solution adjusted as closely as possible to give a neutral reaction showed that this behaved quite differently from the other solutions: already after one day, flocs appeared in the solution. Colorimetric analysis was able to account for only 7% of the original amount of silicic acid.

In order to investigate the effect of the chlorides of sodium, calcium, and aluminum on the rate of conversion of silicic acid into the colorimetrically undeterminable form, four series of solutions were prepared. In all these solutions the silicic acid concentration was $5 \cdot 10^{-4}$ g/ml; acidities of 0.1 N, 0.5 N, and 1 N were employed. Also, solutions of the second series contained $4 \cdot 10^{-2}$ g/ml of NaCl, those of the third series contained $4 \cdot 10^{-2}$ g/ml $CaCl_2$, and those of the fourth series $3.8 \cdot 10^{-2}$ g/ml $AlCl_3$.

The results of these experiments, which are shown in Fig. 3, indicate that in solutions of low acidity the presence of salts leads to an increase in the rate at which silicic acid is converted into the colorimetrically undeterminable form and to an increase in the proportion of silicic acid that is to be found in this form. At higher acidities (up to 1 N), the effect of salts is confined to a certain acceleration of the polymerization process; they are practically without effect on the equilibrium state.

We see, therefore, that for each value of the acidity an equilibrium is set up after a certain time between the colorimetrically determinable and undeterminable forms of silicic acid, and this then continues practically unchanged.

The concentration of determinable silicic acid at equilibrium depends, as will be seen from the results given in Table 1, on the acidity of the solution, and does not depend on the initial concentration of silicic acid.

When silicic acid solutions that have not been aged in acid solution are examined colorimetrically, the coloration attains a maximum intensity in 15-20 minutes after addition of the reagents and then remains constant for a definite period of time. We have found, however, that in the determination of silicic acid in aged acid solutions the colorations resulting from the addition of reagents increases constantly in intensity.

In order to investigate this phenomenon, special experiments were carried out, and the results of these are given in Fig. 4. As the solutions aged, the rise in the intensity of color became less marked. Increase in the acidity of the solution also caused a decrease in the rate at which the intensity of color increased. Reduction of the initial silicic acid concentration had a similar effect.

TABLE 1

Equilibrium Concentrations of Colorimetrically Determinable Silicic Acid in Acid Solutions

Conc of SiO_2 (g/ml)	$3 \cdot 10^{-4}$		$5 \cdot 10^{-4}$		$1 \cdot 10^{-3}$		$2 \cdot 10^{-3}$	
Acidity of solution (normality)	Found SiO_2							
	%	g/ml · 10^{-4}	%	g/ml · 10^{-4}	%	g/ml · 10^{-4}	%	g/ml · 10^{-4}
0.1	—	—	87	4.4*	—	—	16	3.2
0.2	—	—	74	3.7*	—	—	14	2.8
0.5	—	—	39	1.95	20	2.03	10	2.00
1.0	~ 50	~ 1.5	27	1.35	14	1.38	7	1.40
2.0	28	0.83	17	0.85	8	0.77	4	0.80
3.0	—	—	9	0.45	—	—	2	0.40

* Equilibrium was not attained.

If the solution is diluted and then kept for several hours before adding the reagents, the intensity of the coloration is somewhat greater than that in solutions to which the reagents are added immediately after the dilution. With increase in acidity or time of aging, this increased-intensity effect becomes appreciably less marked. Since the intensity of color obtained in the colorimetric test on aged acid solutions increases continuously with time, the comparisons between the experiments were always made on the basis of results obtained twenty minutes after the addition of the reagents.

The results of these experiments show that silicic acid undergoes polymerization in acid solution, i.e. it is transformed from the molecularly dispersed to the colloidally dispersed form (which explains the reductions in the amounts of silicic acid found in solution by the colorimetric method). The equilibrium between the molecularly dispersed and the colorimetrically undeterminable colloidally dispersed forms of silicic acid is not stationary, but moves toward a limit determined mainly by the acidity of the medium. Introduction into the solution of ammonium molybdate leads to the binding of the molecularly dispersed silicic acid in the silicomolybdate complex, and, as a result, the equilibrium may be displaced by the conversion of part of the colloidal silicic acid into the colorimetrically determinable form. Since the amount of silicic acid present in the colloidal form is comparatively great, the conversion of a small part of it into the colorimetrically determinable form will cause an appreciable increase in the intensity of color, although the amount now found will nevertheless remain appreciably less than the true silicic acid content.

As the concentration of silicic acid is increased, the amount present in the colloidal form increases, and this circumstance favors a rise in the intensity of color during the course of the determination. On the other hand, increase in acidity and aging of the solution probably lead to the formation of larger complexes that are more difficult to break down, and, as a result, the rate of increase of color intensity diminishes with time. The colorimetric determination does not, of course, permit a strictly quantitative characterization of the ratio of the amounts of molecularly dispersed and colloidally dispersed forms of silicic acid, for the determination itself leads to a certain displacement of the equilibrium between them. It must be remembered also that a continuous series of intermediate states exists in the solution between these extreme states. It is also impossible, therefore, to draw any quantitative conclusions concerning the degree of polymerization of the silicic acid present in the colloidally dispersed condition on the basis of the colorimetric determination.

TABLE 2

Determination of the True Silicic Acid Content of an Aged Acid Solution by Adding Sodium Carbonate and Heating (SiO_2 concentration, $1 \cdot 10^{-3}$ g/ml; acidity as 1 N HCl)

Time (days)	SiO_2 found g/ml · 10^{-3}	
	Direct determination	After addition of soda
1	0.240	1.03
		0.97
2	0.190	1.00
		1.01
5	0.185	1.02
		0.98
10	0.158	1.01
		1.03
15	0.142	0.99
		0.99
24	0.138	1.00
		1.03
30	0.138	1.01
		0.99

TABLE 3

Determination by Adding Caustic Soda and Heating, of the True Silicic Acid Content of an Acid Solution Aged in the Presence of Aluminum. (SiO_2 concentration, $1 \cdot 10^{-3}$ g/ml; Al_2O_3 concentration $5 \cdot 10^{-3}$ g/ml; acidity as 1 N HCl.

Time (days)	SiO_2 found g/ml · 10^{-3}	
	Direct determination	After addition of caustic soda
1	0.26	1.05
		1.05
3	0.20	1.02
		0.98
7	0.18	1.00
		1.00
10	0.16	1.01
		0.99
15	0.16	1.00
		1.00

Nevertheless, comparisons based on the results of colorimetric determinations permit us to draw a number of conclusions concerning the aging of acid solutions of silicic acid and the effect of a number of factors on this aging process. It should be noted also that our conclusions agree well with the electron-microscope investigations of SiO_2 sols carried out by Beresneva and Kargin [4].

It follows, therefore, that the colorimetric determination of silicic acid does not always reveal its true concentration. In order to determine the whole of the silicic acid in solution, irrespective of the form in which it is present, it is necessary to give the solution an additional treatment. Methods are described in the literature based on heating the solution with an addition of $NaHCO_3$ [1] or sodium fluoride [5]. In our work we heated the solutions after the addition of sodium carbonate or caustic alkali. The first method has the advantage that it is easier to obtain sodium carbonate of sufficiently low silicic acid content. On the other hand, the evolution of CO_2 when the solution is made alkaline with sodium carbonate (and all the more with $NaHCO_3$) and when it is reacidified before the determination makes some of the operations difficult, and treatment of the solution with caustic alkali is free from this defect.

TABLE 4

Determination, by Adding Sodium Fluoride, of the True Silicic Acid Content of Acid Solutions Aged in the Presence of Calcium, Aluminum, or Iron Compounds (SiO_2 concentration, $5 \cdot 10^{-4}$ g/ml, acidity as 1 N HCl)

Conc. of interfering substances	Time (days)	SiO_2 found (g/ml · 10^{-4})	
		before treatment with NaF	after addition of NaF
0	4	2.50	5.05
	7	1.75	4.95
	9	1.60	5.00
$1 \cdot 10^{-3}$ g/ml $CaCl_2$	4	2.20	4.90
	7	1.70	4.90
	9	1.50	4.95
$2 \cdot 10^{-3}$ g/ml Al_2O_3	4	2.20	5.00
	7	1.65	4.90
	9	1.40	4.85
$2 \cdot 10^{-3}$ g/ml Fe_2O_3	4	2.40	5.00
	7	1.75	5.10
	9	1.75	4.90

The following is our procedure for the determination of silicic acid when it is partly present in the colorimetrically undeterminable form: the solution under investigation is neutralized in a platinum crucible with a solution of sodium carbonate or caustic alkali, and a further, excess amount is added, sufficient to bring the concentration to 0.1-0.2 N. If the solution contains a large amount of sodium chloride (up to 8%), the amount of alkali added must be increased to give a concentration of 0.5-0.8 N. The pipet used for the alkali must be carefully washed immediately with distilled water, as otherwise high results will be obtained in subsequent determinations. The solution is heated for 8-10 minutes on a water bath, and, after being cooled, it is acidified in the crucible so that the final acidity is about decinormal. It is then transferred to a measuring flask, where, after addition of reagent, it is made up to volume. In the simultaneous blank test, heating is not necessary; the necessary amount of acid is introduced into a measuring flask, the same amount of alkali is added as for the solution under

investigation, and then ammonium molybdate is added. The solutions of sodium carbonate or caustic alkali must be tested for their silicic acid contents and must be kept in paraffined flasks. Silver crucibles may be used instead of platinum, but they must be boiled out with water before a determination to remove traces of silver oxide formed on the surface.

The method was checked on pure silicic acid solutions, and it was found that silicic acid could be quite satisfactorily determined, irrespective of the form in which it was present. In the case of a solution of $1 \cdot 10^{-2}$ g/ml SiO_2 in 1 N HCl, we found that even when the solution, as a result of aging, acquired a strong opalescence, colorimetric determination after treatment with sodium carbonate gave correct results. As an example we will give the determination of silicic acid during the course of the aging of one of the solutions (Table 2). The agreement of the results obtained with the initial concentration is satisfactory, although direct determination gave very low values.

We obtained similar results also for all the other concentrations of silicic and hydrochloric acids. The method was found to be accurate within approximately $\pm 3\%$.

The question becomes a much more complicated one when, in addition to silicic acid, compounds of other elements are present in the solution. The method of converting silicic acid into a colorimetrically determinable form must then be selected taking into consideration the behavior of the individual elements during the treatment given to the solution. For example, correct results are not obtained when the solution contains aluminum and is treated with sodium carbonate, because the aluminum hydroxide that is then precipitated prevents complete conversion of the silicic acid into the colorimetrically determinable form (part of it being carried down with the precipitate). However, addition of caustic alkali in amount sufficient for the complete dissolution of the aluminum hydroxide makes it possible to obtain quite satisfactory results. Some of the results obtained in this case are given in Table 3.

Treatment of the solution with caustic alkali does not always give satisfactory results: it is not applicable when the solution contains ions that are precipitated by caustic alkali (iron, titanium, manganese, etc.). We therefore, carried out experiments on the conversion of silicic acid into the colorimetrically determinable form with the aid of sodium fluoride, which reacts with polymerized SiO_2 molecules in an acid medium forming fluosilicic acid, which is able to react with ammonium molybdate. The excess of fluoride ions, which interfere in the determination of silicic acid, must be fixed by addition of boric acid or aluminum ions.

The experiments were carried out as follows: the solution containing silicic acid in the colorimetrically undeterminable form (about 12 ml) was placed in a small paraffined beaker, and 2 N HCl (1.2 ml) and a 2.3% solution of sodium fluoride (1.5 ml) were added. After ten minutes, a solution (2.5 ml) containing $3 \cdot 10^{-3}$ g/ml $AlCl_3$ (to bind the excess of fluorine ions) and 5% ammonium molybdate (2 ml) were added; the solution was transferred to a 25 ml measuring flask, made up to volume, and examined colorimetrically. Our method differs from that described in the literature [5] in that all operations are carried out at room temperature. The results given in Table 4 show that this procedure enables silicic acid to be determined in acid solutions in presence of calcium, aluminum, and iron salts.

SUMMARY

1. In acid solutions, polymerization of silicic acid occurs, and this results in a reduction in the amount that can be found by colorimetric analysis. An equilibrium between molecularly dispersed and colorimetrically undeterminable forms of silicic acid is established in accordance with the acidity of the medium. The presence in the solution of sodium, calcium, or aluminum chloride increases the rate at which equilibrium is established, but is practically without effect on its position.

2. In the colorimetric analysis of solutions containing silicic acid partly in the undeterminable form, a continuous increase with time in the intensity of color is to be observed. This is to be explained by the partial displacement of the equilibrium in the direction of the molecularly dispersed form brought about by the addition of ammonium molybdate.

3. In order to determine silicic acid in those cases when it is present in solution in the polymeric form, it is necessary first to convert it into the molecularly dispersed form. In order to achieve this we have heated the solutions with sodium carbonate or with caustic alkali, and we have also made use of addition of sodium fluoride at room temperature. All three methods gave quite satisfactory results. The choice of one or another of these methods depends on the nature of the other substances present in solution.

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LIMITING CURRENTS ASSOCIATED WITH THE CATALYTIC DISCHARGE OF HYDROGEN IONS IN PRESENCE OF AMINES

COMMUNICATION 1. THEORY OF LIMITING CATALYTIC CURRENTS ASSOCIATED WITH THE DISCHARGE OF HYDROGEN IONS

S. G. Mairanovsky

The term "catalytic evolution of hydrogen" is to be understood as the discharge of hydrogen ions at an electrode at potentials that are less negative than those usually required at the given electrode and at the given pH. The catalytic current results from the lowering of the overvoltage in presence of certain substances, i.e. catalysts.

A large number of investigations has been devoted to the experimental study of catalytic hydrogen waves at the dropping mercury electrode. Kolthoff and Lingane in their monograph [1] have made a review of work published up to 1940 on the catalytic action of a number of alkaloids and of substances containing a thiol group. A considerable number of alkaloids has been investigated polarographically by Kirkpatrick [2], and the catalytic evolution of hydrogen in presence of nicotinamide and other pyridine derivatives has been studied in detail by Knobloch [3], who found that the variation of the height of the catalytic wave with catalyst concentration follows an equation that is analogous to Langmuir's adsorption isotherm. He suggested that the catalytic current is proportional to the amount of catalyst adsorbed on the electrode. Experiment shows that when the concentration of catalyst in the solution reaches a certain value the height of the catalytic wave attains a maximum value and remains constant when the concentration is increased further. Knobloch attributes this effect to the complete saturation of the surface of the dropping electrode with catalyst molecules. It is not clear, however, why differing numbers of catalyst molecules are required for the filling of one and the same surface at various concentrations of the proton donor. Knobloch did not explain also the departure that he had observed of the theoretically calculated current from that found experimentally for low concentrations of catalyst.

The Soviet worker Stromberg [4] was the first to make use of the concept of kinetic and adsorption restrictions on the limiting current in order to describe the catalytic waves of hydrogen. His theory explains the behavior of the catalytic system: substance having a thiol group — metal ions — complex-former. Stromberg, however, gave no quantitative experimental confirmation of this theory.

A large amount of factual material has been collected on the catalytic evolution of hydrogen, but investigations of the catalytic current have been carried out over an insufficiently wide range of proton-donor and catalyst concentrations. This has made it impossible to develop a theory that would explain all the phenomena to be observed in the catalytic discharge of hydrogen ions.

We have investigated the relations between the limiting catalytic current and donor and catalyst concentrations over wide ranges of values, and, on the basis of the results, we have made an attempt to give a quantitative interpretation of the regularities observed. In these considerations we have taken the kinetics into account of those processes [5] which, in our opinion, take place at the surface of the dropping mercury electrode.

In the present paper we give the theory of limiting catalytic currents. The experimental results will be given in a later communication.

Derivation of Equations for Limiting Catalytic Currents

The catalytic current usually has a greater value than that to be expected for a simple process of catalyst molecule discharge, limited by diffusion. Every catalyst molecule, therefore, must deal with several proton-donor ions.

The mechanism of the catalytic discharge of hydrogen ions at the dropping mercury electrode may be represented as follows. The catalyst, which exists in two forms in equilibrium — Brønsted's acid and basic forms, BH^+ and B — has the role of proton carrier:

$$B + DH^+ \underset{k_g}{\overset{k_1}{\rightleftharpoons}} BH^+ + D, \qquad (1)$$

The acid form of the catalyst BH^+ accepts electrons from the cathode and is converted into a discharged complex consisting of the basic form carrying a hydrogen atom (BH):

$$BH^+ + e^- \longrightarrow BH. \qquad (II)$$

There follows a process that results in the formation of a hydrogen molecule and regeneration of the catalyst in the basic form:

$$2BH \xrightarrow{k_2} 2B + H_2 \qquad (III)$$

If there are proton-donor ions DH^+ at the electrode surface, they will react with the basic form of the catalyst according to Equation I in an effort to re-establish the equilibrium concentration of the acid form, which is quickly discharged at the electrode, the whole cycle is then repeated. The values of the constant for the equilibrium between the acid and basic forms and the constant k_1 for the rate of formation of the acid form depend on the nature of the catalyst and of the proton donor. The constant k_2 depends only on nature of the catalyst. It will be obvious that the catalytic effect can occur only when the acid form of the catalyst is discharged at a lower negative potential than the proton donor.

The rates of the changes in concentration of the individual forms of the catalyst at the surface of the dropping electrode are described by the following equations:

$$\frac{d[B]_s}{dt} = \frac{\kappa_B}{s\sqrt{}} [B]_0 - \frac{[B]_s}{a_B} + k_2[BH]_s^2 - k_1 [B]_s [DH^+]_s + k_2[BH^+]_s [D]_s. \qquad (1)$$

$$\frac{d[BH^+]_s}{dt} = \frac{\kappa_{BH^+}}{sF} \left([BH^+]_0 - \frac{[BH^+]_s}{a_{BH^+}} \right) + k_1[B]_s [DH^+]_s - \frac{i}{sF} - k_2 [BH^+]_s [D]_s, \qquad (2)$$

$$\frac{d[BH]_s}{dt} = \frac{i}{sF} - k_2[BH]_s^2 - \frac{\kappa_{BH}}{sFa_{BH}} [BH]_s. \qquad (3)$$

In these equations $[Z]_0$ and $[Z]_s$ are the bulk and surface concentrations of the substances; $\kappa_Z = 607\, D_Z^{1/2} m^{2/3} t^{1/6}$ is the constant of the Ilkovič equation; s is the mean surface of the dropping electrode; F is the faraday; a_Z is the constant for the equilibrium between the surface and bulk concentrations of the substance [6]:

$$a_Z = \frac{[Z]_s}{[Z]_0}, \qquad (4)$$

and i is the catalytic current.

An analogous equation can be written for the proton donor:

$$\frac{d[DH^+]_s}{dt} = \frac{\kappa_{DH^+}}{sF} \left([DH^+]_0 - \frac{[DH^+]_s}{a^*_{DH^+}} \right) - k_1[B]_s [DH^+]_s + k_2 [BH^+]_s [D]_s. \qquad (5)$$

In this equation $a^*_{DH^+}$ is not a constant, the point being that the concentration of proton donor is generally many times as great as the concentration of catalyst (often of quite a different order), and it frequently attains fairly high values (up to 0.1 M). In this case it is necessary to take into account the part of the surface occupied by the proton donor, and for the expression of its surface concentration the Langmuir equation must be used; thus:

$$a^* = \frac{a_{DH^+}}{1 + b[DH^+]_0}. \qquad (6)$$

At low values of $[DH^+]_0$ the value of $a^*_{DH^+}$ coincides with that of a_{DH^+}, which is a constant (Henry's constant).

When constant conditions are established at the surface of the drop, we have

$$\frac{d[Z]_s}{dt} = 0. \qquad (7)$$

For a limiting catalytic current there will be a further supplementary relationship: the concentration of the acid form at the electrode surface will fall to zero, which is described by the equation

$$[BH^+]_s = 0. \qquad (8)$$

Adding Equations 1, 2, and 3, while taking Equations 7 and 8 into account, we obtain

$$[B]_s = \frac{a_B}{\kappa_B}\left(\kappa_B[B]_0 + \kappa_{BH^+}[BH^+]_0\right) - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s. \tag{9}$$

For practical purposes we may consider [6] that

$$\kappa_B = \kappa_{BH^+}, \tag{10}$$

and we then have

$$[B]_s = a_B\left([B]_0 + [BH^+]_0\right) - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s = a_B[K]_0 - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}\,[BH]_s, \tag{11}$$

where $[K]_0$ is the general (analytical) concentration of catalyst in the solution.

For the surface concentration of proton donor we obtain from Equations 2 and 5:

$$[DH^+]_s = \frac{a^{\bullet}_{DH^+}}{\kappa_{DH^+}}\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0 - i\right). \tag{12}$$

Substituting the values for $[B]_s$ and $[DH^+]_s$ in Equation 2, and taking the conditions expressed in Equations 7 and 8 into account, we find that:

$$\frac{1}{sF} = \frac{\kappa_{BH^+}}{sF}[BH^+]_0 + \frac{k_1 a_B a^{\bullet}_{DH^+}}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0 - i\right), \tag{13}$$

whence

$$i = \frac{\kappa_{BH^+}[BH^+]_0 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left(\kappa_{DH^+}[DH^+]_0 + \kappa_{BH^+}[BH^+]_0\right)\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)} \tag{14}$$

Taking into account the fact that the catalyst concentration is usually a hundred or a thousand times lower than the proton-donor concentration, i.e. that

$$[K]_0 \ll [DH^+]_0, \tag{15}$$

we may neglect the magnitude of the diffusion current for the acid form of the catalyst $\kappa_{BH^+}[BH^+]_0$ both in comparison with the magnitude of the diffusion current of the proton donor (the term $\kappa_{DH^+}[DH^+]_0$) and in comparison with the catalytic current, i.e. with the second term of the numerator of Equation 14. The expression for the magnitude of the limiting catalytic current will then take the form:

$$i = \frac{k_1 a_B a^{\bullet}_{DH^+}sF\,[DH^+]_0\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \dfrac{k_1 a_B a^{\bullet}_{DH^+}sF}{\kappa_{DH^+}}\left([K]_0 - \dfrac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)} \tag{16}$$

A similar expression is obtained when, as is often the case, the catalytic wave precedes the wave for the reduction ("hydrogenation") of the catalyst itself.

Let B' and $B'H^+$ be the basic and acid forms of the unreduced catalyst. If we assume that the acid form, owing to the difference in charges, is more readily reduced, then at the electrode, the following processes precede the catalysis:

$$B' + DH^+ \xrightarrow{k_4} B'H^+ + D \tag{IV}$$

and

$$B'H^+ + (n-1)\,H^+ + ne^- \xrightarrow{i_{hydr.}} B. \tag{V}$$

In acid solution the catalyst is present mainly in the acid form, and for the diffusion wave associated with "hydrogenation" of the catalyst we may write

$$i_{hydr.} = n\kappa_B[K]_0. \tag{17}$$

The factor n is introduced because in Equations 1, 2, and 3 κ_B took only the rate at which the substance was presented into account and n was assumed to be unity.

Equations I, II, and III will be correct for the catalytic process. The rate of change in the concentrations of the individual substances at the cathode will be given by the equations:

$$\frac{d[B]_s}{dt} = \frac{i_{hydr.}}{nsF} + k_3[BH]_s^2 + k_2[BH^+]_s[D]_s - k_1[B]_s[DH^+]_s - \frac{\kappa_B}{sF}\frac{[B]_s}{a_B}, \tag{18}$$

$$\frac{d[BH^+]_s}{dt} = k_1[B]_s[DH^+]_s - \frac{i}{sF} - k_2[BH^+]_s[D]_s - \frac{\kappa_{BH^+}}{sF}\frac{[BH^+]_s}{a_{BH^+}}, \tag{19}$$

$$\frac{d[BH]_s}{dt} = \frac{i}{sF} - k_3[BH]_s^2 - \frac{\kappa_{BH}[BH]_s}{sFa_{BH}}, \tag{20}$$

$$\frac{d[DH^+]_s}{dt} = \frac{\kappa_{DH^+}}{sF}\left([DH^+]_0 - \frac{[DH^+]_s}{a^\circ_{DH^+}}\right) - k_1[B]_s[DH^+]_s - \frac{i_{hydr.}}{sF} + k_2[BH^+]_s[D]_s. \tag{21}$$

By taking the conditions expressed in Equations 7 and 8 into account we obtain from Equation 19:

$$i = k_1 sF\,[B]_s\,[DH^+]_s. \tag{22}$$

It follows from Equations 18, 19, 21, and 22 that:

$$[B]_s = \frac{i_{hydr.}}{n}\frac{a_B}{\kappa_B} - \frac{\kappa_{BH}a_B}{\kappa_B a_{BH}}[BH]_s \tag{23}$$

and

$$[DH^+]_s = a^\circ_{DH^+}[DH^+]_0 - \frac{a^\circ_{DH^+}}{\kappa_{DH^+}}(i + i_{hydr.}). \tag{24}$$

Substituting Equations 23 and 24 in Equation 22, we find

$$\frac{i}{sF} = k_1 a_B a^\circ_{DH^+}\left([DH^+]_0 - \frac{i + i_{hydr.}}{\kappa_{DH^+}}\right)\left(\frac{i_{hydr.}}{n\kappa_B} - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right) \tag{25}$$

and

$$i = \frac{k_1 a_B a^\circ_{DH^+} sF\left([DH^+]_0 - \frac{n\kappa_B[K]_0}{\kappa_{DH^+}}\right)\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \frac{k_1 a_B a^\circ_{DH^+} sF}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}. \tag{26}$$

If Equation 15 holds, then, neglecting $n\kappa_B[K]_0/\kappa_{DH^+}$ in comparison with $[DH^+]_0$, we obtain:

$$i = \frac{k_1 a_B a^\circ_{DH^+} sF[DH^+]_0\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}{1 + \frac{k_1 a_B a^\circ_{DH^+} sF}{\kappa_{DH^+}}\left([K]_0 - \frac{\kappa_{BH}}{\kappa_B a_{BH}}[BH]_s\right)}. \tag{27}$$

It will be readily seen that Equation 27 is identical with Equation 16.

In Equations 16 and 27 the value of the concentration $[BH]_s$ remains undetermined. An expression for $[BH]_s$ can be readily found from Equation 3:

$$[BH]_s^2 + \frac{\kappa_{BH}[BH]_s}{k_3 a_{BH} sF} - \frac{i}{k_3 sF} = 0. \tag{28}$$

and therefore

$$[BH]_s = -\frac{\kappa_{BH}}{2k_3 a_{BH} sF} + \sqrt{\left(\frac{\kappa_{BH}}{2k_3 a_{BH} sF}\right)^2 + \frac{i}{k_3 sF}}. \tag{29}$$

Only the positive sign is to be taken before the root, since the value of $[BH]_s$ cannot be a negative one. Allotting symbols to the constants:

$$\frac{\kappa^2_{BH}}{2k_3 s \sqrt{a^2_{BH} \kappa_B}} = r \text{ and } \frac{4k_3 a^2_{BH} sF}{\kappa^2_{BH}} = p, \qquad (30), (31)$$

we find that the expression $[BH]_s$ takes the form:

$$[BH]_s = \frac{\kappa_B a_{BH}}{\kappa_{BH}} \cdot r\left(\sqrt{1+ip}-1\right) \qquad (32)$$

Substituting the expression for $[BH]_s$ from Equation 32 and that for $a^{\circ}_{DH^+}$ from Equation 6 into Equation 16, we obtain a general equation relating the value of the catalytic current to the concentrations of the components of the solution:

$$i = \frac{k_1 a_B a_{DH^+} sF \kappa_{DH^+} [DH^+]_0 \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}}{\kappa_{DH^+}(1 + b\ [DH^+]_0) + k_1 a_B a_{DH^+} sF \left\{[K]_0 + r\left(\sqrt{1+ip}-1\right)\right\}}. \qquad (33)$$

It is necessary to remember that for very low values of the ratio $[DH^+]_0 / [K]_0$ (10-100 or less), when the condition in Equation 15 does not operate, it is no longer possible to neglect the diffusion current for the discharge of the basic form of the catalyst or its "hydrogenation" current. It is then necessary to employ not Equation 33, but Equations 14 or 26, substituting in these the values of $a^{\circ}_{DH^+}$ and $[BH]_s$ from Equations 6 and 32. A low value of $[DH^+]_0 / [K]_0$ is met in polarographic practice when working with catalytic waves in solutions of high pH. In this case the proton donor (most frequently the acid salt of a polybasic acid, or an ammonia buffer, in which the donor is NH_4^+) is fairly inert, and the rate (k_1) of its reaction with the catalyst is not great. Hence, in order to obtain values of the catalytic current that are convenient for measurement it is necessary to increase the concentration of the catalyst considerably.

Case of High Proton-Donor Concentrations

As a subsequent communication will show, for sufficiently high values of the ratio $[DH^+]_0 / [K]_0$ the catalytic current does not depend on the concentration of the donor in the solution. The surface concentration of the donor is so great in this case that it covers an appreciable proportion of the electrode surface, and, owing to the low concentration of catalyst, the removal of donor from the surface due to catalytic discharge is not considerable.

If the concentration of acid is very much greater than that of catalyst, then in the denominator of Equation 33 we may neglect the terms κ_{DH^+} and $k_1 a_B a_{DH^+} sF \left\{[K]_0 - r(\sqrt{1+ip} - 1)\right\}$ in comparison with $b \cdot \kappa_{DH^+} [DH^+]_0$. The expression for the catalytic current then takes the form:

$$i = \frac{k_1 a_B a_{DH^+} sF}{b} \left\{[K]_0 - r(\sqrt{1+ip}-1)\right\} \qquad (34)$$

or

$$i = Q\left\{[K]_0 - r\left(\sqrt{1+ip} - 1\right)\right\}, \qquad (35)$$

in which

$$Q = k_1 a_B a_{DH^+} sF / b. \qquad (36)$$

If at low catalyst concentrations the acid concentration is not sufficiently high, so that we may neglect only the term $k_1 a_B a_{DH^+} sF \left\{[K]_0 - r\left(\sqrt{1+ip}-1\right)\right\}$ in the denominator of Equation 33, then this equation will take the form:

$$i = \frac{k_1 a_B a_{DH^+} sF\ [DH^+]_0}{1 + b[DH^+]_0} \left\{[K]_0 - r\left(\sqrt{1+ip} - 1\right)\right\}, \qquad (37)$$

or

$$i = Q'\left\{[K]_0 - r\left(\sqrt{1+ip} - 1\right)\right\}, \qquad (38)$$

where

$$Q' = \frac{b[DH^+]_0}{1 + b[DH^+]_0} Q. \qquad (39)$$

Conditions corresponding to this case are found in experiments in 0.05 N HCl, the results of which are given in the subsequent communication.

As will be shown, the value of the constant $\underline{p}$ for quinine is of the order of 10^5 microamp^{-1}. The two terms of unity in Equation 38 may therefore be neglected in comparison with the magnitudes of $\underline{ip}$ and $\sqrt{ip}$, for at currents of not less than 1 microamp we have

$$ip \gg 1 \quad \text{and} \quad \sqrt{ip} \gg 1 \tag{40}$$

so that

$$i = Q([K]_0 - \sqrt{i^2 ip}) \tag{41}$$

The equation for the current derived from Equation 41 is

$$i = Q'[K]_0 + \frac{(Q')^2 i^2 p}{2} - \sqrt{\frac{(Q')^4 i^4 p^2}{4} + (Q')^3 i^2 p [K]_0} \tag{42}$$

The derivative of the current with respect to the catalyst concentration has the form:

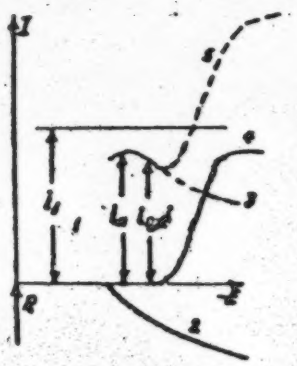
$$\frac{di}{d[K]_0} = Q - \frac{(Q')^3 i^2 p}{\sqrt{(Q')^4 i^4 p^2 + 4(Q')^3 i^2 p [K]_0}} \tag{43}$$

and the slope of the curve $i = \underline{f}([K]_0$ therefore rises with increase in quinine concentration and tends toward the value Q.

Form of the Catalytic Wave

A peculiar feature of catalytic waves is the presence on them of a convexity having a flat maximum followed by a concave depression. Catalytic waves do not change in character when surface-active substances are added to the solution. The nature of the maximum, therefore, is not associated with the movement of the mercury surface of the dropping electrode, but arises from the nature of the catalytic effect itself.

It should be noted that it has been assumed in this paper, as also in other papers cited [1,2,3], that the value of the limiting catalytic current corresponds to the height of the catalytic wave at its maximum. This assumption is a convenient one when catalytic waves are used for analytical purposes, but it is not theoretically justified. The catalytic wave can be represented as the sum of three curves (see Figure). Curve 1 is the "original" catalytic wave of the usual form. To this we must add algebraically Curve 2, which represents the dependence of $R = k_1 a_B a_{DH^+} sF$, on the potential (possible changes in the value of $\sqrt{i^2 p}$ with potential may be neglected, for $\underline{ip}$ is a constant, and the effect of the added constant $\sqrt{i}$ is negligible). This relationship may be expressed in the form $R = Ae^{-\beta(E_0 - E)}$ where E_0 is the potential at which R has its maximum value and E is the cathode potential; A and β are constants. The superposition of Curves 1 and 2 determines the form of the catalytic wave. If the usual discharge of the proton donor does not follow immediately after the catalytic discharge. If immediately after the catalytic discharge there follows the usual discharge of the proton donor, which has not been discharged catalytically, then on the catalytic wave 3 there is superimposed the wave for the discharge of donor remaining on the electrode surface (Curve 4). A rise sets in on the catalytic curve (Curve 5), which goes over into the wave of the proton donor.



Scheme illustrating the form of the catalytic wave: 1) "original" catalytic wave; 2) curve of R against E; 3) catalytic wave without superposition of the discharge current of the donor; 4) wave for the discharge of the donor; 5) summation wave.

The value of the limiting catalytic current is a function of the potential, and its greatest value i_1 corresponds to maximum R. The current at the maximum of the observable wave, i_m, forms a certain proportion of i_1, and the ratio i_1/i_m depends on the relation between the concentrations of catalyst and donor. At high values of $[K]_0$, $[DH^+]_0$, as follows from equation 46, change in R is practically without effect on the value of the limiting current, which is determined by supply of donor. The wave then does not have a maximum, and i_1/i_m has a minimum value. At low values of $[K]_0$, $[DH^+]_0$ the wave for the usual discharge of the donor begins at less negative potentials; the beginning of the rise fully compensates for the fall in the curve due to the fall in R, and the wave has the form of the usual S-shaped curve. The catalytic wave itself, however, which is obtained from the total wave by subtraction of the donor wave, shows its usual fall.

The author takes this opportunity of expressing his great indebtedness to M. B. Neiman for his constant interest in the work, and also to A. N. Frumkin for valuable suggestions.

SUMMARY

1. A kinetic interpretation has been given of the phenomena observed in the catalytic discharge of hydrogen ions.

2. Relationships have been derived between the value of the limiting catalytic current and the concentrations of the components of the solution.

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CONDITIONS FOR THE IGNITION OF GAS MIXTURES

COMMUNICATION 22. EFFECT OF ADDITIONS OF DIETHYL PEROXIDE AND ACETALDEHYDE ON THE KINETICS OF COOL-FLAME OXIDATION OF BUTANE

A. A. Dobrinskaya and M. B. Neiman

In a series of investigations, Neiman, Tutakin, Blat, and Gerber [1, 2] have studied the effect of the addition of diethyl peroxide on the period of induction of the butane cool flame. It was shown that the induction period for the butane cool flame depends on the amount x of added peroxide, the relationship being expressed by the following equation:

$$K_1\tau = a - \ln x. \qquad (1)$$

Neiman and coworkers [3, 4] have shown that this equation is applicable to the oxidation of propane and of dimethyl ether. Similar results were obtained by Egerton and Harris [5] in an investigation of the effect of diethyl peroxide on the induction period for the propane cool flame.

In the present investigation we have set ourselves the task of studying in greater detail the effect of diethyl peroxide on the process of cool-flame oxidation of butane and also of the effect on this process of acetaldehyde, the kinetics of the formation of active products during the induction period being investigated in each case. Studies of the kinetics, in absence of additives, of the build-up of active intermediate products during the period of induction of the butane cool flame have also been made previously [6, 7].

EXPERIMENTAL

Experimental Procedure

a) Description of apparatus. Apart from some minor modifications, the procedure followed was the same as that described in detail in previous papers [6, 7]. The cool flame was obtained by admitting a mixture of butane and oxygen into a previously evacuated quartz vessel heated to a definite temperature; the formation of flame was observed visually. Induction periods were determined with the aid of a stop watch. Analytical tests on the gaseous reaction mixture were made as follows. At a definite time the gaseous mixture was allowed to pass from the reaction vessel to an intermediate flask, and was slowly pumped off through a U-tube cooled by liquid oxygen. The condensed reaction products were then warmed and blown out with a stream of hydrogen into a train of two absorption vessels. The solutions were then analyzed polarographically for their content of organic peroxides and aldehydes [8-13].

b) Preparation and purification of the starting materials. Butane was prepared by the hydrogenation of 2-butene; it was purified from unsaturated hydrocarbons and tested for organic peroxides and aldehydes in the manner described in the literature [5]. Diethyl peroxide was prepared from diethyl sulfate and 12% hydrogen peroxide [14]. Diethyl sulfate (105 parts) and hydrogen peroxide (125 parts) were carefully mixed together in a flask at 15°. A 5% solution of KOH (180 parts) was added dropwise to the mixture. Reaction proceeded under careful cooling for six hours, and the reaction products were then fractionated on an oil bath. The fraction boiling between 55° and 76° was collected and was washed with a 30% solution of NaOH and with water in order to remove alcohol and ether. The diethyl peroxide obtained was repeatedly distilled; the fraction boiling between 63.5° and 65° was used in the experiments. The refractive index (n_D^{18}) of diethyl peroxide was found to be 1.37014, a value in good agreement with that found by Neiman, Blat, and Gerber, namely $n_D^{18} = 1.37009$ [2].

Measurements were made also of the vapor pressure of diethyl peroxide at various temperatures. The latent heat of vaporization of diethyl peroxide calculated from these results was $\lambda = 7400$ cal/mole, in good agreement with the value of $\lambda = 7300$ cal/mole obtained by Blat [2]. Acetaldehyde CH_3CHO was prepared by the depolymerization of pure paraldehyde, and was carefully fractionated. The fraction boiling at 20° was used in the experiments. In order

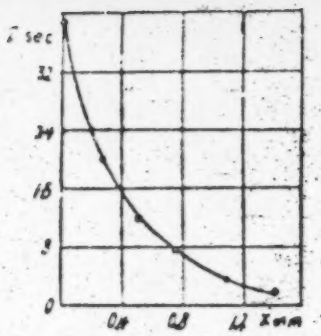

Fig. 1. Effect of addition of diethyl peroxide on the induction period for the butane cool flame.

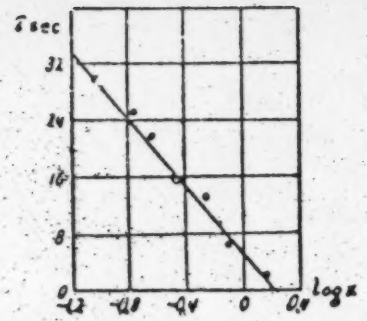

Fig. 2. Relation between the induction period for the butane cool flame and the concentration of diethyl peroxide.

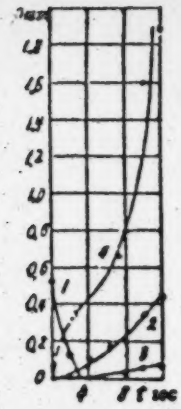

Fig. 4. Changes in the contents of diethyl peroxide (1), peroxides A and B (2 and 3), and aldehydes (4) during the induction period for the mixture $C_4H_{10} + O_2 + 0.5$ mm $(C_2H_5O)_2$ at 310° and 333 mm.

to avoid the formation of peroxides, the acetaldehyde was kept in sealed ampoules in absence of oxygen. Before an experiment, qualitative tests for peroxides were made and the results were always negative. Oxygen and hydrogen were prepared by the electrolysis of a 15% solution of NaOH, and they were then purified as indicated in previous papers [6, 7].

EXPERIMENTAL RESULTS

1. Effect of Addition of Diethyl Peroxide on the Kinetics of Cool-Flame Oxidation of Butane

a) Shortening of the induction period due to addition of diethyl peroxide. We investigated the shortening of the induction period resulting from addition of diethyl peroxide at 310° and 333 mm. As will be seen from the curve (Fig. 1) as the addition of diethyl peroxide was increased, the period of induction was reduced in a regular manner.

In order to verify Equation 1, we plotted the experimental results with $\log x$ and τ as coordinates (Fig. 2), and within the limits of experimental error, the experimental points fall on a straight line, as required by Equation 1. From the slope of this line we find $K = 0.009$.

b) Build-up of peroxides and aldehydes. We investigated the build-up of peroxides and aldehydes during the induction period, the reaction being carried out in presence of diethyl peroxide. In this series of experiments, carried out at 310° and 333 mm, an addition of 0.54 mm of diethyl peroxide was made to the butane-oxygen mixture. The amounts of peroxides and aldehydes were determined by a polarographic method, as described above. The results of our analyses are represented in Fig. 3.

It will be seen from Fig. 3 that the concentration of diethyl peroxide rapidly fell immediately after the admission of the mixture into the heated vessel. Simultaneously peroxides, which were reduced at -0.2 and -0.1 V (Curves 2 and 3) and aldehydes (Curve 4) began to accumulate in the mixture. The decomposition of diethyl peroxide resulted in the appearance of appreciable amounts of aldehydes, and many initiating centers were evidently formed. As as result, the oxidation reaction was accelerated.

2. Effect of Addition of Acetaldehyde on the Kinetics of Cool-Flame Oxidation of Butane

a) Shortening of the induction period due to addition of acetaldehyde. It has been shown by the work of Alvazov and Neiman [15] that addition of acetaldehyde leads to a shortening of the period of induction of the pentane cool flame. We have investigated the effect of addition of acetaldehyde on the period of induction of the cool flame of butane at 333 mm and 310°. As the addition of CH_3CHO was increased, the induction period for the cool flame was reduced in a regular manner (Fig. 4). Addition of CH_3CHO in amounts appreciably in excess of that which, according to our analyses, builds up by the end of the induction period, although shortening the induction period, did not eliminate it completely. Newitt and Thorne's hypothesis [16], according to which the cool flame arises as a result of the building up of a critical concentration of aldehydes, is therefore evidently incorrect.

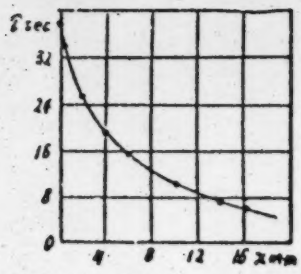

Fig. 4. Effect of addition of acetaldehyde on the kinetics of cool-flame oxidation of butane

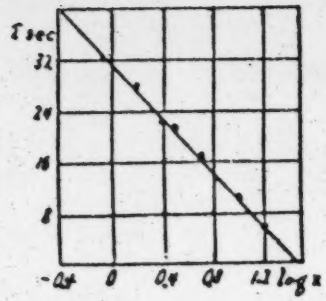

Fig. 5. Relation between the period of induction of the butane cool flame and the concentration of acetaldehyde

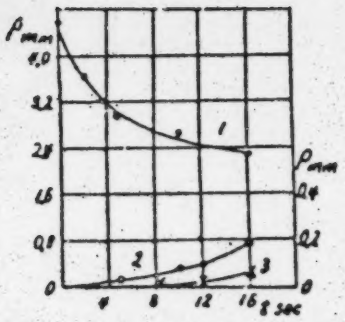

Fig. 6. Changes in the concentrations of aldehydes (1) and peroxides that are reduced at -0.25 and -0.6 V (2 and 3) during the induction period in the mixture C_4H_{10} (101 mm) + O_2 + $(C_2H_5)_2$ (2 mm) at 320° and 333 mm.

The relation between the induction period and the amount of added aldehyde [Ald] closely accords with the equation:

$$\log [Ald] = b - 0.4343\, K_2 \tau \qquad (2)$$

as will be seen from Fig. 5, in which the experimental results are plotted with log [Ald] and τ as coordinates. The experimental points lie on a straight line, and it follows from the value of the slope of this line that b in Equation 2 has the value 0.1. The shortening of the induction period for the butane cool flame due to addition of acetaldehyde therefore follows the same law as that found for additions of diethyl peroxide.

The good quantitative agreement between the coefficients K_1 and K_2 of Equations 1 and 2 should be noted. The constants a and b in these equations differ in value.

b) Changes in the concentrations of peroxides and aldehydes. We have carried out a series of experiments with the mixture $C_4H_{10}+O_2$ in presence of 4.5 mm of acetaldehyde. In these experiments the pressure and temperature of the mixture were 333 mm and 320° respectively. The results of peroxide determinations for these conditions are given in Fig. 6. An examination of Fig. 6 will show that as the concentration of aldehyde in the mixture fell there was a simultaneous accumulation of peroxides, which were reduced at -0.25 and -0.6 V. The latter was formed to about double the extent of the former.

DISCUSSION OF RESULTS

We will examine the possible mechanism of cool-flame induction by additives. Our experiments give us reason to suppose that, when a certain amount of diethyl peroxide is added, the latter decomposes with formation of the peroxides A and B (which are reduced at -0.2 and -1.0 V).

We will suppose that the initial concentration of the peroxide formed is proportional to the rate of decomposition of diethyl peroxide, for which the constant is k_1; we may then write:

$$[Per]_0 = k_1[Per]_0' \qquad (3)$$

We shall make the same assumption in the case of the acetaldehyde addition. Let the constant for the decomposition of the aldehyde be k_2; the initial concentration of the peroxide will then be expressed in Equation 4:

$$[Per]_0 = k_2[Ald]_0 \qquad (4)$$

Blat, Gerber and Neiman [2] suppose that during the induction period there is a slow autocatalytic reaction, in the course of which active oxidation products are formed. The rate of formation of active products is expressed by the equation:

$$\frac{d[Prod]}{dt} = K[Prod] \qquad (5)$$

The cool flame arises when the concentration of active products attains a value termed by the authors "critical."

TABLE 1

Comparison of the rates of decomposition of acetaldehyde and diethyl peroxide added to a mixture of butane and oxygen at 310°

% decomp	Time of decomp (sec): t_{Ald}	t_{Per}	$\frac{t_{Ald}}{t_{Per}}$
25	3	0.2	15
33	6	0.4	15
50	20	1.2	16

TABLE 2

Comparison of the effectiveness of acetaldehyde and diethyl peroxide with respect to the shortening of the induction period of the butane cool flame

t(sec)	Addition of aldehyde(mm)	Addition of peroxide (mm)	$\frac{Ald}{Per}$
32	0.9	0.06	15
24	2.5	0.16	15
16	5.8	0.36	16
8	12.8	0.75	17
4	19.5	1.15	17

Let us suppose further that the initial concentration of active products is $[Prod]_0$; then, integrating Equation 5, we obtain.

$$\ln \frac{[Prod]_c}{[Prod]_0} = K\tau \qquad (6)$$

The active product may be a peroxide formed from the added diethyl peroxide.

Substituting the value of $[Per]_0$ from Equation 3 in Equation 6, we obtain:

$$\ln \frac{[Per]_c}{k_1[Per]_0} = K\tau. \qquad (7)$$

In a similar way, substituting the value of $[Per]_0$ from Equation 4 in Equation 6, we obtain:

$$\ln \frac{[Per]_c}{k_2[Ald]_0} = K\tau. \qquad (8)$$

From Equations 7 and 8 we shall determine the ratio of the peroxide and aldehyde concentrations that shorten the induction period to an equal extent.

If we treat the values of τ in Equations 7 and 8 as identical, we obtain by equating the left-hand side of these equations

$$\ln \frac{[Per]_c}{k_1[Per]_0} = \ln \frac{[Per]_c}{k_2[Ald]_0} \qquad (9)$$

It follows from this that there will be equal shortening of the period of cool-flame induction when the concentrations of the added aldehyde or peroxide are inversely proportional to their decomposition constants:

$$\frac{[Ald]_0}{[Per]_0} = \frac{k_1}{k_2} \qquad (10)$$

The ratios of the rate constants for the decompositions of acetaldehyde and diethyl peroxide may be determined from the ratio of the intervals of time during which these substances decompose to a definite extent.

$$\frac{k_1}{k_2} = \frac{t_2}{t_1} \qquad (11)$$

In Table 1 the intervals of time are given during which diethyl peroxide and acetaldehyde, admitted into a mixture of $C_4H_{10} + O_2$ decompose to the extent of 25%, 33%, and 50%. It can be seen from Table 1 that

$$\frac{t_{Ald}}{t_{Per}} = \frac{k_1}{k_2} \approx 15. \qquad (12)$$

This means that under the conditions of the experiments described the peroxide decomposes about fifteen times as rapidly as acetaldehyde

In Table 2, the amounts of aldehyde and peroxide are given which shorten the induction period for the cool flame to an equal extent.

The data on which Table 2 is based are taken from Figures 1 and 4.

As may be seen from Table 2:

$$\frac{[Ald]}{[Per]} \approx 16 \qquad (13)$$

The value of the ratio $\frac{[Ald]}{[Per]}$ calculated from our experiments coincides, within the limits of experimental error, with the ratio of their decomposition rates, as will be seen by comparing Equations 12 and 13.

The mechanism we have proposed for the shortening of the period of induction of the cool flame in presence of active additives is therefore able to give a satisfactory explanation of the observed facts.

SUMMARY

1. It has been shown that addition of diethyl peroxide to a butane-oxygen mixture reduces the period of induction of the cool flame.

2. When the additive is diethyl peroxide, organic peroxides and aldehydes are formed in the mixture during the induction period.

3. It has been shown that the addition of acetaldehyde shortens the period of induction of the butane cool flame. Organic peroxides, which are reduced at -0.25 and -0.6 V, are formed in the mixture.

4. Addition of an amount x of peroxide or aldehyde reduces the induction period τ in accordance with the law:

$$\log x = b - k\tau.$$

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NEW APPARATUS FOR MEASURING SORPTION

E. N. Nikitin

The high accuracy of sorption measurements, which has been attained largely as a result of the work of Academician M. M. Dubinin's school [1,2], permits satisfactory determinations to be made of the surface and porosity of gels and fine powders. Sorption measurements are carried out at the present time almost exclusively by a gravimetric or volumetric method in which a high vacuum is employed. Improvement in sorption apparatus has proceeded on the one hand in the direction of particularly sensitive balances, permitting the registering of changes in the weight of sorbent of less than 10^{-5} g; and on the other hand, the efforts of experimentalists have been directed toward the devising of apparatus for volumetric sorption measurements based on the measurement of pressure changes resulting from introduction of sorbent. The lower limit of applicability for the gravimetric method is determined by the sensitivity and capacity of the quartz spiral. The volumetric method has a wider range of applicability; it is most useful for the investigation of the surface area and porosity of sorbents of low activity.

Numerous designs for sorption apparatus have been published [3]. Below we give a description of yet another apparatus of simpler design, which, in our view, enables volumetric sorption measurements of increased accuracy to be made. Simplification of apparatus accompanied by increased accuracy should encourage the introduction of sorption technique into laboratory practice.

Volumetric Sorption Apparatus

The proposed apparatus combines in itself the elements of a McLeod gage, a U-type manometer, a gas buret, and a thermostated tube for sorbent (Fig. 1). Unlike existing apparatus [3], this device has no capillary communicating tubes: capillary tubes impede evacuation so much that it is probably rare for the adsorbent to be freed from sorbed impurities [4]. The principle on which the apparatus works is a generally accepted one and is based on the determination of the pressure change occurring in a space when a sorbent is introduced into it.

Mercury from the reservoir R can pass into the gage and compress gas in the left limb to a volume corresponding to a position in the capillary K. The mercury in the right limb will therefore stand at a higher level than in the left limb. The position of the mercury can be fixed with the aid of a stainless steel rod, the end of which is ground to act as a stopper. The volumes of the capillary and the left limb are determined by filling with mercury, so that the apparatus can serve as a McLeod gage.

In order that the apparatus may be used as a U-type manometer having a renewable vacuum, it is sufficient for the mercury to be raised about half-way in the two limbs. As the sorption measurements are carried out at a strictly constant volume, there is a sealed-in platinum contact at C. When the mercury comes in contact with the platinum, an electric circuit is closed and a small neon lamp flashes. The elevation of the mercury in the left limb is measured with the aid of a cathetometer fitted with a microscope and mechanical indicator I.

The whole space in the right limb above the fused-in contact is surrounded by a glass jacket A_1, through which water is circulated from an ultrathermostat. The volume of the space, V_1, is determined by filling with mercury, and this space may therefore act as a substitute for a gas buret. The tube containing adsorbent, V_2, may be connected to, or disconnected from the thermostated space V_1 by means of a tap. The volume of the tube V_2 is also determined by filling with mercury. While measurements are in progress, the tube V_2 is thermostated by surrounding it with the small glass jacket A_2; during evacuation the jacket A_2 is replaced by the tubular nichrome heater H.

In the upper part of the apparatus there is a three-way tap, which enables the apparatus to be connected either to the vacuum main or to a tube containing the liquid to be sorbed (e.g. methanol, ethanol, water, etc.). Glass inserts are placed in the nonthermostated tubing; these are intended to reduce the volume of nonthermostated space.

When graduating the apparatus it is convenient to determine the volumes in the left limb before the apparatus is attached to the evacuation system. The volumes V_1 and V_2 are determined by removing mercury with the aid of a Drechsel bottle attached to a water pump. This operation must be preceded by thorough evacuation of the whole

apparatus followed by complete filling of the whole appratus with mercury (including the tube for the sorbent).

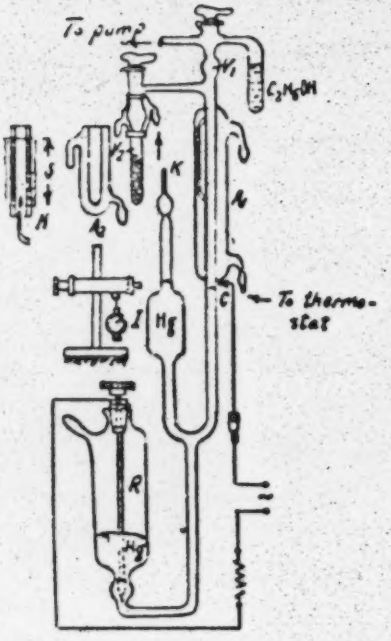

Fig. 1 Volumetric Sorption Apparatus.

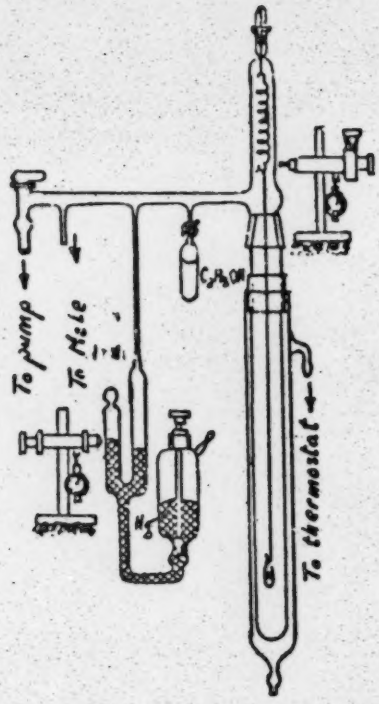

Fig. 2. Diagram of Sorption Balance.

The technique of sorption measurements is fairly simple. Prior to the experiment the whole apparatus, including the tube containing the sorbent, is carefully evacuated. Then, by turning the taps, the spaces V_1 and V_2 are disconnected, and into the first of these a certain amount of vapor is introduced. The mercury in the right limb is brought into contact with the platinum (when the neon lamp flashes) and the pressure of the vapor, P_1, is measured. The spaces V_1 and V_2 are then connected together by turning the tap, and a part of the vapor passes in to fill the tube V_2 and part is absorbed by the sorbent. The mercury is again brought to the contact, and the equilibrium pressure P_2 of the vapor is measured. From the gas laws we may calculate the loss of vapor due to absorption by the sorbent:

$$P_1V_1 = P_2(V_1 + V_2 + V_{ads.}). \qquad (1)$$

In spite of its simple construction, the apparatus gives results of high accuracy and reliability. This is achieved because of the following improvements: 1) absence of capillary communicating tubes; 2) reduction in the error due to inaccuracy of graduation (V_1 and V_2); 3) reduction of nonthermostated space to a minimum; 4) increase in accuracy of measurement of pressure owing to the use of an electric contact; 5) reduction of number of taps in the apparatus to a minimum.

The degree of accuracy attainable may be judged from the fact that we have obtained reproducible isotherms for the sorption of ethanol vapor by the walls of the empty tube. The apparatus is very convenient in use, and the time taken by an experiment is considerably shortened, owing to the following circumstances: 1) evacuation is rapid, owing to the shortness and width of the communicating tubes; 2) for the same reason sorption equilibrium is attained rapidly; 3) use of the plunger closing device enables raising and lowering of the mercury to be carried out rapidly.

Choice of Optimum Dimensions for the Spiral of a Sorption Balance

In the measurement of sorption by the gravimetric method a sorption balance is used, and one of the essential features of such a balance is a spiral of fine quartz thread. A diagram of a sorption balance is given in Fig. 2; it is

unnecessary here to explain the purpose served by the various components. The accuracy of weighing depends on the choice of the dimensions of the spiral. The choice of these dimensions is generally made on the basis of "empirical considerations". We are not aware, however, of any experiments or calculations carried out for this purpose. It is an open question whether it is an advantage to use extremely fine quartz threads for making the spirals. The capacity of a balance constructed from very fine threads would be extremely low, and it would not be possible therefore, to weight a sample of perceptible weight on such a balance.

It will be readily seen that the quality of a balance spiral is determined by the product of the capacity* and the sensitivity**; this quantity will also be a measure of the accuracy of weighing***. In order, therefore, to decide which of two spirals is the better (i.e. the more accurate), it is necessary to calculate the capacity and sensitivity in each case and then multiply these quantities together; the spiral for which this product is the greater will be the more accurate. If spiral A is twice as sensitive as spiral B, but the capacity of the first is half that of the second, then for weighing purposes, evidently, the two spirals will be equivalent, the only essential difference being that spiral A will be more prone to accidental breakage, being constructed from finer thread.

In the construction of spirals, it is necessary to make the number of turns as great as possible, for sensitivity can then be increased without reduction in capacity. The number of turns is generally limited by the length of the thread, which is often determined by the length of the sweep of the glass blower's arm. In practice it is not necessary to obtain very long threads; the individual spirals can be hooked together in a string.

It is shown in courses on the strength of materials [5] that the extension of a spiral is related to its dimensions by the equation:

$$\frac{\lambda}{P} = \frac{4R^3n}{Gr^4}, \qquad (2)$$

where λ is the extension of the spiral (mm); P is the load (g); $\frac{\lambda}{P}$ is the sensitivity of the spiral (mm/g); R is the radius of a turn of the spiral; r is the radius of the thread, n is the number of turns (taken as 10 under the conditions of our problem), G is the shear modulus for quartz, which, according to our determinations, is $0.24 \cdot 10^7$ g/sq.mm. The maximum permissible load on the spiral, below which elongation is proportional to load, is related to the dimensions of the spiral by the equation:

$$P_{max} = \frac{\pi \sigma r^3}{2R}, \qquad (3)$$

where P_{max} is the maximum permissible load (capacity) for the spiral (g), and σ is the permissible shearing load for quartz, which, according to our measurements, is $0.265 \cdot 10^4$ g/sq.mm.

The values of G and σ were found from three experiments with quartz spirals, mean values being taken. The value of G was found by substitution of the values of R, r, and n (obtained from measurements on the spirals) in Equation 2; the values of λ and P were taken from the calibration curves****. The value of σ was found by substitution of values of R and r in Equation 3. The value of P_{max} was again taken from the calibration curves.

By the use of Equations 2 and 3 we calculated the sensitivities and capacities of quartz spirals of various dimensions, the number of turns being ten in each case. The results are given in the table, in which at intersections of R-columns and r-rows the following figures are given:

Multiplicand — capacity of spiral (g)
Multiplier — sensitivity (mm/g)
Product — which is a measure of the accuracy of weighing

For example, a spiral for which the radius of a turn is R = 8 mm and the radius of the thread is r = 0.1 mm has a sensitivity of 85 mm/g and a capacity of 0.334 g, while the product of these quantities, which is a measure of the quality of the spiral, is 28.3 mm. It will be seen from the table that another spiral, for which R = 50 and r = 0.2, has a sensitivity of 1300 mm/g and a capacity of 0.668 g. In general, other things being equal, weighing with

* Capacity is to be understood as the limiting load applied to the spiral beyond which the linear relation between elongation and load no longer applies.

** Sensitivity is to be understood as the elongation (mm) of the spiral produced by a load of 1 g.

*** Accuracy of weighing is to be understood as the ratio expressed as percent of the absolute error to the weight of the sample.

**** The calibration curves for the spirals, i.e. plots of $\lambda = f(P)$, are not given in the text.

TABLE 1

r mm → / ↓	R = 6 R^3 = 216	R = 8 R^3 = 512	R = 10 R^3 = 1000
r = 1	0.0036 X 250 = 0.9	0.0085 X 334 = 2.83	0.0166 X 416 = 6.9
r = 0.5	0.057 X 32.3 = 1.84	0.136 X 41.5 = 5.65	0.265 X 52.0 = 13.8
r = 0.2	2.25 X 2.0 = 4.5	5.33 X 2.67 = 14.3	10.4 X 3.34 = 34.6
r = 0.1	36 X 0.25 = 9.0	85 X 0.334 = 28.3	166 X 0.416 = 69.0
r = 0.05	572 X 0.0323 = 18.4	1360 X 0.0415 = 56.5	2650 X 0.052 = 138
r = 0.02	22,500 X 0.002 = 45.0	53,300 X 0.00267 = 143	104,000 X 0.00334 = 346

NOTE: The multiplicand is the capacity of the spiral (g); the multiplier is the sensitivity (mm/g).

$$P_{max} = \frac{\pi \sigma r^3}{2R} \quad ; \quad \frac{\lambda}{P} = \frac{4R^3 n}{Gr^4}$$

$G = 0.24 \cdot 10^7$ g/sq. mm; $\sigma = 0.265 \cdot 10^4$ g/sq.mm; n = 10 turns

the aid of the second spiral will give results that are 30.7 times as accurate as those obtained with the aid of the first.

An analytical investigation shows, therefore, that increase in the accuracy of weighing may be achieved not so much by reduction in the thickness of the thread, as by increase in the radius of a turn of the spiral. Finally, we have checked our calculations experimentally for glass spirals of various dimensions. This experimental test has fully confirmed the conclusion that for the purpose of weighing it is desirable to use fine spirals in which the radius of a turn of the spiral is high. The correct choice of the dimensions of the quartz spiral used in a balance may lead to a several-fold increase in the accuracy of weighing, a matter of considerable importance in the study of sorption processes.

SUMMARY

1. An apparatus is described for the measurement of sorption by the volumetric method. It is simple to construct and enables sorption measurements to be made with high accuracy.

2. The optimum dimensions of a quartz spiral for a sorption balance have been calculated. The calculations show that the accuracy of weighing can be increased not so much by reduction in the thickness of the thread, as by increase in the radius of a turn of the spiral.

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Table 1

R = 12	R = 14	R = 20	R = 50
R^3 = 1728	R^3 = 2444	R^3 = 8000	R^3 = 125,000
0.0284 X 346 = 9.8	0.0405 X 296 = 12	0.133 X 208 = 27.7	208 X 83.2 = 173
0.459 X 43.5 = 20	0.645 X 37 = 23.8	2.12 X 26 = 54.8	33.2 X 10.4 = 346
18.0 X 2.77 = 50	25.4 X 2.37 = 60	83 X 1.67 = 138	1300 X 0.668 = 870
284 X 0.346 = 98	405 X 0.296 = 120	1330 X 0.208 = 277	20,700 X 0.0832 = 1730
4590 X 0.0435 = 200	6450 X 0.037 = 238	21,200 X 0.026 = 548	332,000 X 0.0104 = 3460
180,000 X 0.00277 = 500	254,000 X 0.00237 = 600	830,000 X 0.00167 = 1380	13,000,000 X 0.000668 = 8700

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HYDROTECHNICAL CEMENTS IN THE CENTRAL ASIAN REPUBLICS*

I. S. Kantsepolsky

Resolutions carried at the Nineteenth Congress of the Party have set responsible and honorable tasks for scientific workers and for workers in the silicate industry.

For some years the silicate chemistry laboratory of the Institute of Chemistry, Uzbek Acad. Sciences, has studied local mineral raw material with the aim of producing water-stable and sulfate-stable cements. It is known that the ability of many binding materials to harden in water is based on the formation of sparingly soluble hydrosilicates and hydroaluminates of calcium. Among all the known binding substances, aluminous cement shows the greatest propensity to undergo hydraulic hardening. Portland cement occupies the second place. Present-day chemistry and technology permits the preparation of a cement having a strength approximating to that of a natural stone, such as marble, but when we bring about improvement in the mechanical strength of cement, its deficiencies become more and more pronounced, for they depend on the very essence of the hardening process. Cement consists essentially of : $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. As a result of detailed investigation of the hydration, hydrolysis, and hardening processes for individual clinker minerals and cements, it has been established that tricalcium silicate, the principal mineral present in cement clinker causing the hydraulic hardening of the cement, undergoes hydrolysis, under the action of the limited amount of water required for the formation of a plastic dough, with formation of a less basic hydrogel of calcium orthosilicate and with separation of free lime. Dicalcium silicate undergoes hydration very slowly and forms a hydrogel of calcium orthosilicate. Tricalcium aluminate undergoes hydration forming tetracalcium hydroaluminate.

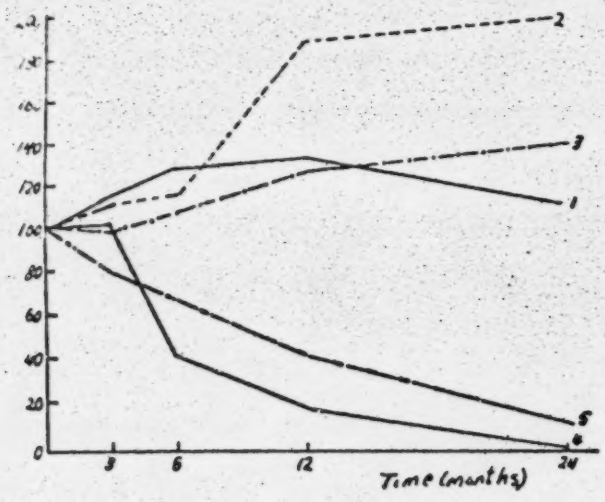
The question of the hydrolysis and hydration of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ remains an open one. Thus, of all the minerals present in cement clinker, only $3CaO \cdot SiO_2$ undergoes hydrolysis with separation of free lime. The content of $3CaO \cdot SiO_2$ in present-day cement may be as high as 70%. Hence in cement that has undergone prolonged hydration, much lime accumulates—up to 15%. The formation of a crystalline concretion of calcium hydroxide under conditions that preclude its dissolution constitutes a positive factor in the hardening of cement; but under the action of large amounts of water, as occurs in hydrotechnical construction, the lime is leached out, and the more rapidly this occurs, the less compact the concrete will be. The leaching of free lime leads to hydrolysis of the other products of the hardening of cement mortars and concretes. In fresh water, however, the disruption of hydrotechnical structures occurs only slowly, entirely owing to the formation of a protective film of calcium carbonate, which delays the diffusion of water through the outer surface; but it is not possible for the protective crust to prevent the leaching of lime completely, since its thickness, even after prolonged hardening, attains a value of only 5-10 mm.

In his classical work on hydraulic cements, Baikov [1] has shown that these cements can give stable systems under natural conditions only when an appreciable proportion of the lime present is able to be converted into carbonate before it is leached out in the free condition or bound in the form of silicates and aluminates. Baikov has concluded, therefore, that hydrotechnical structures of Portland cement are bound to be disrupted, owing to the leaching of the lime. Although in fresh waters, owing to the formation of a compact concrete (which is associated with the use of large amounts of cement), hydrotechnical structures made from Portland cement last for many decades, in mineralized sulfate waters the disruption process proceeds fairly rapidly. Sulfates act on tetracalcium hydroaluminate with formation of calcium sulfoaluminate. The crystals of calcium sulfoaluminate, formed by combination with the original solid phase of 3 molecules of gypsum and 31 molecules of water, occupy a considerably greater volume than $4CaO \cdot Al_2O_3 \cdot aq$. Stresses arise which lead to the disruption of the hydrated cement.

The theoretical concepts that we have outlined concerning the hardening of Portland cement are confirmed by its behavior in various media (see the figure). Cement hardens best in an atmosphere saturated with water vapo

* Paper read at a conjoint session of the Division of Chemical Sciences of the USSR Academy of Sciences and the Academy of Sciences of the UzbekSSR held on 25th of October, 1962 in Tashkent.

...in this medium the best conditions obtain for the hydration of the cement. The increase in strength from 28 days to 2 years is 1.3% (Curve 2). In spite of the exceptionally severe conditions that we specially created for the hardening of cement in the air (the samples were transferred to the air after they had been hardened for only one day in a damp place) the samples showed a smooth rise in strength, whereas the samples kept in water showed no further rise after six months. In a 5% solution of Na_2SO_4 the cement had already lost 65% of its strength in six months, and after two years had become a formless mass (Curve 5). In a sulfate solution close in composition to the corrosive subsoil waters of Bukhara, the cement constantly lost in strength and was practically destroyed after two years. Thus, Portland cement, which is a very effective binding material for above-ground construction, cannot rationally be used in hydrotechnical construction and is completely unusable in mineralized sulfate waters.



Change in the strength of Portland cement when hardened in different media (as a percentage of the strength of a 28-day-old cement). 1) in water; 2) damp atmosphere; 3) in air; 4) in a 5% Na_2SO_4 solution; 5) in Bukhara water.

In order to obtain high-grade water-stable and sulfate-stable cements, it is essential to follow the road laid down by the elder generation of Soviet scientists Baikov [1], Druzhinin [2], Kind [3], Yung [4], and Budnikov [5]: free lime must be bound by active silica to give difficultly soluble calcium hydrosilicate. As numerous investigations have shown, the composition of calcium hydrosilicate depends on the pH of the solution, and, when sufficient active silica is present calcium metasilicate is formed, which gives a limiting CaO concentration at 30° of 0.052 g per liter. The solubility of lime in presence of active silica is therefore reduced thirty-fold.

Hence, as Baikov has shown, the carbonation of lime in presence of sufficient active silica occurs before it can dissolve. Incidentally, it should be noted that Baikov's remarkable idea—that the hardening process in hydraulic cements constitutes, in effect, the formation of calcium carbonate—was first confirmed experimentally by Myakinchenko [6], a scientist of our laboratory, working with glinite cement. It was established that, everything considered, the hydraulic hardening of glinite cement did actually amount to the formation of calcium carbonate. In presence of a sufficient amount of active silica, sulfate attack on Portland cement is also eliminated. Although the introduction of hydro additives does not prevent the formation of calcium sulfoaluminate, disruption of the hydrated cement does not occur in presence of sufficient amorphous silica. Yung [7] explains this by the deposition of the calcium sulfoaluminate, formed under these conditions through the liquid phase, in the pores of the cement, without disruption of its structure. This explanation often encounters great difficulties.

Numerous investigations in our laboratory have shown that the content of free lime in samples immersed in a sulfate medium may attain 7%. In presence of such a large amount of free lime, tetracalcium hydroaluminate cannot undergo hydrolysis. We consider that the mechanism of the formation of calcium sulfoaluminate in cement with hydro additives is the same as that operating in cement without hydro-additives. The formation of calcium sulfoaluminate in these cements occurs through the solid phase by the direct combination of calcium sulfate with insoluble tetracalcium aluminate.

We explain the sulfate-stability of cement in presence of sufficient active silica by the favorable conditions for the crystallization of calcium sulfoaluminate in an elastic medium, rich in colloidal formations.

Thanks to extensive investigations by Soviet scientists, beginning from 1930 here in the Soviet Union, the production of a new hydrotechnical cement, called pozzolanic Portland cement, has been established. This hydrotechnical cement is obtained by the introduction of hydraulic additives to Portland cement clinker before grinding. The widest application has been obtained by pozzolanic Portland cements having additions of tripolite, which contains

much active silica. The great experience gained in the mass production and varied application of this cement, and also the wealth of experimental material that has accumulated in research institutes, has enabled a clear picture of the value and defects of pozzolanic Portland cement to be formed. While having considerable advantages over Portland cement with respect to water-stability and sulfate-stability, pozzolanic cements have a number of defects Pozzolanic cements, owing to the slow interaction of the active silica with lime and their high water demand harden more slowly than Portland cements. Also, pozzolanic cements are less resistant than Portland cements to the alternate action of water and frost.

For this reason, the building material section of the committee set up by the Presidium of the USSR Academy of Sciences for coordination with the construction of hydro-stations, canals, and irrigation systems (chairman: Bodnarkov) has recommended the use of three types of cement for hydrotechnical concrete, according to the hardening conditions of the concrete or ferroconcrete in the structures. For concretes and ferroconcretes that are subjected to the systematic action of water and frost, it is recommended that a cement without hydro-additives and having a C_3A content of not greater than 5% should be used. For the interior of massive concrete and ferroconcrete, pozzolanic Portland cement is recommended the C_3A content of the original cement should not be greater than 7%. For concretes and ferroconcretes on the outer parts of structures, a cement having a C_3A content of up to 8% is recommended up to 10% of hydro-additives is permissible. Such is the general position of the question of hydrotechnical cements.

In the Central Asian Republics there is a great need for sulfate-stable cements, which results from the high degree of mineralization of the subsoil waters in a number of districts. Having regard for the urgency of this question, the silicate chemistry laboratory, as already indicated, has for some years been making a study of local mineral raw materials with the object of preparing water-stable and sulfate-stable cements.

The most promising additives for the pozzolanization of Portland cement to be found in the Central Asian Republics are the natural burnt clays. These clays are now called by the name introduced by the geologist Tsybyshev: "gliezh". Gliezhes were formed as the result of subterranean coal fires and are found in all the districts of Central Asia in which coal deposits occur. The gliezhes of Kzyl-Ki have been studied in the greatest detail [8]. In their chemical and mineralogical composition, gliezhes are fairly homogeneous and consist of burnt kaolinite clays in which an appreciable amount of sand is incorporated. As the question of the use of glinite for the preparation of sulfate-stable cement had not been solved, we paid special attention to the question of the effect of gliezh on the sulfate-stability of cement.

As a result of these investigations the question of the effect of glinite on the sulfate-stability of cement, which has been in dispute for a long time, has been definitely settled. It has been shown that it is possible to prepare sulfate-stable cements from glinite by two methods [9]: the first method consists in the preparation of sulfate-stable cements by the introduction into Portland cement of glinite prepared by roasting kaolinite clays to give complete dehydration of the kaolinite (600-800°).

In this case, as a senior scientist of our laboratory, Tashpulatov, showed [10], a sulfate-stable pozzolanic Portland cement is obtained by using the usual proportions of cement and hydro-additive (60% cement + 40% glinite). Although Yung, our acknowledged specialist on cements, treats with skepticism the possibility of preparing sulfate-stable pozzolanic Portland cements from glinite [7], we consider that scientifically based facts will prevail and that the glinite Portland cement developed by Tashpulatov will find wide application in mineralized sulfate waters.

The second method, developed by the author in conjunction with Galkina and Myakinchenko, consists essentially in the introduction into Portland cement of glinite prepared by roasting kaolinite clays at the temperature of the transition of silica from the amorphous to the crystalline condition (900-1000°). This method, being the most readily applicable for gliezhes, has indeed been the basis for the manufacture of pozzolanic Portland cement in the cement works of the republic. The limiting amount of active silica in the gliezh is 3.5%. Gliezh having this active-silica content increases the sulfate-stability of the cement in proportion to the amount added. The best proportions of cement and gliezh from the point of view of sulfate-stability is 30% of Portland cement and 70% of gliezh, since only with such proportions is the whole of the lime separating during the hardening of the cement taken up by the gliezh.

Gliezh, by its ability to give lime the property of hardening in water, is to be considered as an active hydraulic additive that is inferior to Bryansk tripolite only in the degree in which these properties are shown By the introduction of up to 30% of gliezh we appreciably improved the water-stability and sulfate stability of cement.

Investigations over many years of the properties of gliezh and of gliezh Portland cement, experience in its

TABLE 1

Chemical and Mineralogical Compositions of Cements Obtained under Manufacturing Conditions

Name of cement	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Other radicals	H_2O at 105°
Cement VF	21.40	4.30	6.00	0.27	64.62	1.68	0.40	0.65	0.20
Cement F	22.35	5.31	5.81	—	63.90	1.62	0.61	0.18	0.23
Cement A	21.62	5.24	4.48	0.27	65.75	1.59	0.72	0.68	0.12
Cement V	21.79	4.75	2.94	0.29	67.15	1.71	0.02	0.53	0.27

TABLE 2

Chemical Composition of Artificially Prepared Aggressive Waters

Composition of solution	Solution No. 1	Solution No. 2	Solution No. 3	Solution No. 4	Solution of 0.59% Na_2SO_4	Solution of 1.18% Na_2SO_4	Solution of 3% Na_2SO_4
Temporary hardness	30°	14°	—	—	—	—	—
pH	7	7	—	—	—	—	—
Free CO_2 mg/liter	127	43	—	—	—	—	—
HCO_3 mg/liter	660	305.0	—	—	—	—	—
Ca mg/liter	350	265.2	421	562	—	—	—
Mg mg/liter	600	132.4	746	837	—	—	—
Cl mg/liter	1,920	1695.0	1,020	2,141	—	—	—
SO_4 mg/liter	4,480	1382.4	5,489	7,462	4,000	8,000	20,282
Na (by difference), mg/liter	2,104	1318.3	1,388	2,738	1916	3,833	9,718
Total ions, mg/liter	10,114	5098.3	9,064	13,740	5,916	11,833	30,000
$Ca(HCO_3)_2$ mg/liter	876	405	—	—	—	—	—
$CaSO_4$ mg/liter	455	561	1,431	1,910	—	—	—
$MgSO_4$ mg/liter	2,964	662	3,730	4,140	—	—	—
Na_2SO_4 mg/liter	2,655	675	2,222	4,160	5,916	11,833	30,000
NaCl mg/liter	3,164	2795	1,681	3,530	—	—	—
Total salts	10,114	5098.3	9,064	13,740	—	—	—

mass production and experience in its application in various constructional work have shown that gliezh is a valuable and reliable hydraulic additive. Owing to the use of gliezhes, the cement works of the republic produce every year tens of thousands of tons more high-quality cement.

The question of the manufacture of high-quality, water-stable, sulfate-stable, frost- and atmosphere-resisting, and low-temperature cements has taken on national economic significance. A number of research institutes in our country are working on this problem, and our laboratory also is trying to solve this nationally important problem. We have set ourselves the task of increasing the sulfate-stability of cement and of pozzolanic Portland cement by changing the mineralogical composition of cement clinker. With this in view, one of the scientists of our laboratory, Zhabitsky, has synthesized a number of cements from calcium carbonate, silica gel, silica, and ferric oxide, differing in their mineralogical compositions. The sulfate-stability was examined in accordance with the demands made by technical conditions for hydrotechnical concrete (GOST 4798-49).*

The method consisted essentially in establishing the limiting bending strength of samples of the cement investigated when hardened in aggressive solutions or in drinking water. As a quantitative characteristic of stability, the stability coefficient (SC_6) of the cement in the given medium was taken. SC_6 is the ratio of the mean limiting bending strength for prisms of the given cement after six months' hardening in the aggressive solution to the mean limiting bending strength for prisms of the same cement after six-months' hardening in drinking water. The water under test (the medium) was regarded as aggressive to concrete made from the given cement if SC_6 was not less than 0.8. The samples to be examined for sulfate-stability were transferred, after a preliminary hardening for fourteen days in water, to a 3% solution of sodium sulfate, which is very characteristic in its aggressive action.

* GOST = All-Union State Standard.

Table 1

Σ	Free CaO	Calculated mineralogical composition (%)					KH	$\frac{SiO_2}{Al_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
		C_3S	C_2S	C_3A	C_4AF	$C_3A + C_4AF$			
99.52	0.28	62	15	2	18	20	0.92	2.02	0.73
100.01	0.08	44	31	4	18	22	0.84	2.01	0.91
100.47	0.15	55	23	7	14	21	0.89	2.16	1.23
99.45	0.22	70	9	8	9	17	0.95	2.74	1.68

TABLE 3

Analysis of Samples of Cement Hardened in 3% Na_2SO_4 Solution (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.49	17.96	11 06	6.90
"	2	0.85	20.53	13.27	7.26
"	3	Traces	26.52	18.13	8.39
"	6	"	29.37	21.28	8.09
Cement VF with 30% gliezh	1	1.18	13.77	7.48	6.29
"	2	0.33	13.79	6.39	7.40
"	3	0	17.42	10.64	6.78
Cement VF with 50% gliezh	1	0.37	9.87	3.43	6.44
"	2	Traces	9.99	3.01	6.98
"	3	0	9.78	3.40	6.38
"	6	0	9.53	4.52	5.01
Cement A	1	2.25	22.51	14.53	7.98
"	2	0.40	22.96	14.41	8.55
"	3	Traces	31.53	22.93	8.60
"	6	"	30.72	20.19	10.53
Cement A with 30% gliezh	1	0.46	13.39	6.92	6.47
"	2	Traces	14.53	6.68	7.85
"	3	"	15.93	8.59	7.34
"	6	"	15.75	8.46	7.29
Cement A with 50% gliezh	1	0.26	9.35	3.72	5.63
"	2	Traces	8.95	2.74	6.21
"	3	"	9.91	3.86	6.05
"	6	"	6.60	2.58	4.02
Cement V	1	3.05	19.00	9.15	9.85
"	2	1.37	27.45	13.48	13.97
"	3	1.23	28.00	16.48	11.52
"	6	0.24	30.46	20.25	10.21
Cement V with 50% gliezh	1	0.42	13.08	6.42	6.66
"	2	0.55	11.05	2.96	8.09
"	3	0.44	10.69	2.58	8.11
"	6	0.11	10.71	3.07	7.64
Pozzolanic Portland cement with tripolite	1	1.20	13.50	6.15	7.35
"	2	0.77	14.40	7.16	7.24
"	3	0.37	13.75	6.53	7.22
"	6	0.10	15.31	6.81	8.50

TABLE 3

Analysis of Samples of Cement Hardened in Aggressive Solution No. 1 (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.95	7.17	2.14	5.03
"	2	2.13	7.33	2.24	5.09
"	3	Traces	7.94	3.16	4.78
"	6	0	8.36	3.47	4.89
Cement VF with 30% gliezh	1	1.33	6.10	1.46	4.64
"	2	0.58	6.05	1.42	4.63
"	3	0.14	6.55	2.07	4.48
"	6	0	7.25	2.68	4.57
Cement VF with 50% gliezh	1	0.24	6.82	2.01	4.82
"	2	0	7.33	1.82	5.51
"	3	0	8.48	3.11	5.37
"	6	0	9.87	4.67	5.20
Cement A	1	3.45	9.92	4.06	5.86
"	2	—	12.56	5.54	7.02
"	3	1.26	12.51	5.90	6.61
"	6	—	13.81	6.83	6.98
Cement A with 30% gliezh	1	0.38	8.76	3.09	5.67
"	2	0.29	9.43	3.26	6.17
"	3	Traces	11.31	4.55	6.76
"	6	"	11.20	4.61	6.59
Cement A with 50% gliezh	1	0.11	6.7	1.34	5.42
"	2	Traces	7.07	1.54	5.53
"	3	0	9.16	3.50	5.66
"	6	0	8.13	2.14	5.99
Cement V	1	3.11	8.74	3.07	5.67
"	2	—	11.99	4.54	7.45
"	3	1.60	12.51	4.37	8.14
"	6	0.16	14.75	4.32	10.43
Cement V with 50% gliezh	1	—	8.00	2.92	5.08
"	2	—	9.35	3.01	6.34
"	3	0.37	9.95	3.42	6.53
"	6	Traces	10.95	4.09	6.86
Pozzolanic Portland cement with tripolite	1	0.65	8.18	2.85	5.33
"	2	Traces	9.33	3.33	6.00
"	3	"	8.90	3.20	5.70
"	6	0	11.59	4.52	7.07

The solution was changed every two months. The results of the investigations show that Portland cement without hydro additives is disrupted by a 3% sodium sulfate solution. the stability coefficient is less than 0.8. Cements of high C_3A content are destroyed particularly rapidly. Pozzolanic Portland cements prepared from cement clinker having a C_3A content of up to 5% withstand the test (SC_6 is not less than 0.8). The results of the laboratory investigations were checked under manufacturing conditions at one of the Uzbekistan cement works. By the addition of ferric slag to the mix we obtained four batches of cement of varying mineralogical composition (Table 1). The cements produced under manufacturing conditions satisfied the technical requirements for high-quality cements. Pozzolanic Portland cements prepared from these cements and containing 30 and 50% of gliezh had compression strengths after a 28 day hardening in water of 300-400 kg/sq cm for rammed mortars and 180-240 kg/sq cm for plastic mortars. A study was made of the effects of additions of gliezh, Darbazin "opoka" (silica-containing clay), and Bryansk tripolite on the frost-resistance of the cement; the chemical composition is given in Table 1 under the designation F. Testing was carried out on plastic mortars (1:3 with Volsk sand). The temperature in the cold room was −14-24°.

TABLE 5

Analysis of Samples of Cement Hardened in Aggressive No. 2 (The results are calculated for the binder and are expressed as a percentage of the roasted sample)

Name of cement	Age (months)	Free CaO	$CaSO_4$		
			total	as gypsum	as sulfoaluminate
Cement VF	1	2.42	7.49	1.32	6.17
"	2	0.79	6.55	0.43	6.12
"	3	—	8.35	2.02	6.33
"	6	—	9.07	2.68	6.39
Cement VF with 30% gliezh	1	1.35	6.27	1.00	5.27
"	2	—	7.92	1.82	6.10
"	3	—	7.04	2.12	4.92
"	6	—	7.97	2.75	5.22
Cement VF with 50% gliezh	1	—	5.30	1.80	3.50
"	2	—	5.66	1.02	4.64
"	3	—	5.72	2.51	3.21
"	6	—	6.06	1.59	4.47
Cement A	1	—	7.39	2.17	5.22
"	2	—	8.21	1.75	6.46
"	3	—	7.88	2.04	5.85
"	6	—	12.45	4.61	7.84
Cement A with 30% gliezh	1	—	6.21	1.26	4.95
"	2	—	6.00	1.05	4.95
"	3	0.11	7.51	2.23	5.28
"	6	0	7.80	2.38	5.42
Cement A with 50% gliezh	1	—	5.90	1.52	4.38
"	2	—	5.70	0.78	4.92
"	3	—	—	—	—
"	6	—	5.66	1.53	4.13
Cement V	1	2.43	6.50	1.16	5.34
"	2	—	—	—	—
"	3	2.27	8.82	1.41	7.41
"	6	0	9.58	2.94	6.64
Cement V with 50% gliezh	1	—	—	—	—
"	2	—	5.98	2.58	3.40
"	3	0.38	7.19	0.98	6.21
"	6	—	—	—	—
Pozzolanic Portland cement with tripolite	1	1.43	4.59	0.93	3.66
"	2	—	—	—	—
"	3	0.72	6.37	0.97	5.40
"	6	—	6.88	1.37	5.51

Portland cement, with and without additions of 15% gliezh, showed great frost-resistance to 100 freezing cycles. Cements having additions of 15% opoka, 15% tripolite, and 30 and 50% gliezh lost from 10 to 27% in strength after 100 cycles (as compared with similar specimens hardened in wet sawdust). A notable deleterious effect on the frost-resistance was produced by Darbazin opoka. A cement containing 15% opoka was equivalent in frost-resistance to a pozzolanic Portland cement containing 50% gliezh. As in the determination of sulfate stability in a 3% solution of Na_2SO_4 by the method given, all the cements produced under laboratory conditions were broken down, irrespective of their C_3A content and basicity; in the determination of the sulfate-stability of cements produced under manufacturing conditions, we used, in addition to 3% Na_2SO_4, salt solutions that were close in composition to the subsoil waters of a number of Central Asian districts. Also, a high-alite cement — aluminoferrite cement VF — was tested in a saturated solution of calcium sulfate and in a Na_2SO_4 solution having SO_4'' content of up to 8000 mg/liter. The chemical compositions of the aggressive waters are given in Table 2.

TABLE 6

Sulfate Stability of Cements Produced under Manufacturing Conditions. Pozzolanic Cements Prepared from them by Addition of Gliezh and Pozzolanic Cement

Name and composition of cement	Milling fineness (%) residue on 900 mesh per sq cm sieve	passed 4900 mesh sq cm sieve	Mixing water (%)	Limiting bending strength of a 1:3.5 mortar (kg/sq cm)																							
				in drinking water							in Solution No. 1						in Solution No. 2						in Na_2SO_4 solution				
				Duration (months)																							
				½	1	2	3	6	9	12	1	2	3	6	9	12	1	2	3	6	9	12	1	2	3	6	9	12
Cement VF	0.5	96.2	8.9	26	30	33	38	33	35	33	34	36	45	42	40	41	33	31	30	32	32	35	28	30	18	16	16*	19*
Cement VF with 30% gliezh	0.4	95.5	8.5	26	34	35	40	44	41	47	38	48	60	55	50	55	36	49	44	47	42	48	39	41	50	27	25	17
Cement VF with 50% gliezh	0.4	95.0	8.1	21	34	37	41	42	46	47	37	49	48	53	51	55	30	45	41	47	56	49	36	44	43	35	22	20
Cement A	0.5	95.9	9.6	25	34	36	38	42	42	41	34	32	33	32	36	36	34	28	26	25	33	36	20	25	22	18	16*	16*
Cement A with 30% gliezh	0.4	95.3	9.3	24	37	38	41	46	42	40	37	47	44	54	52	54	33	36	39	42	36	40	35	37	41	33	24	27
Cement A with 50% gliezh	0.4	94.9	8.2	20	30	33	34	38	39	36	37	42	41	48	48	47	31	36	41	42	40	38	32	40	51	19	25	17
Cement V	0.1	96.3	9.6	31	29	32	37	38	44	35	31	25	29	26	22	20	27	30	29	29	32	33	15	14	14	18*	21*	18*
Cement V with 50% gliezh	0.2	97.6	8.9	21	24	28	36	37	36	39	29	34	45	45	43	44	26	28	35	33	36	33	22	28	29	42	35	25
Pozzolanic Portland cement with Bryansk tripolite	0.4	93.9	10.7	22	27	29	31	41	45	40	36	35	46	48	48	49	29	35	33	35	37	34	36	32	36	43	36	31

TABLE 7

Sulfate-Stability of Cement VF with 50% Added Gliezh in Various Media

Name and composition of cement	Milling fineness (%) Residue on 900 mesh/sq. cm. sieve	Passed 4900 mesh/sq.cm sieve	Mixing water (%)	Limiting bending strength of a 1:3.5 mortar (kg/sq cm)																							
				In drinking water					In saturated $CaSO_4$ solu				In solution No. 3				In solution No. 4				0.58% sol. of Na_2SO_4 **				1.18% sol. of Na_2SO_4 ***			
				Duration (months)																							
				½	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12	1	3	6	12
Cement VF	0.1	98	10	18	26	29	32	35	27	29	34	24	34	32	29	20	31	27	20	20	26	28	31	27	28	32	32	26
Cement VF with 50% gliezh	0.2	96	11.7	20	23	28	35	33	30	34	34	33	29	35	42	39	34	37	43	42	27	35	35	31	29	30	35	35

Parallel with the sulfate-stability determinations we made a study of the kinetics of the accumulation of calcium sulfate and sulfoaluminate during the hardening of cements in aggressive media. Determinations were made also of the amount of free lime in cements hardening in water and in aggressive media (Tables 3, 4, and 5).

If the kinetics of the formation of calcium sulfate and sulfoaluminate in cements hardening in a 3% solution of Na_2SO_4 are examined, the copious accumulation of calcium sulfate in the cements will be obvious. In spite of the large variation in mineralogical composition, the calcium sulfate contents of all the cement samples are practically identical and attain the value of about 30% in six months.

* Asterisks against numbers indicate point at which cracks appeared in the samples.

** (4,000 mg SO_4^{--} per liter).

*** (8,000 mg SO_4^{--} per liter).

The process of calcium sulfate formation proceeds particularly vigorously during the early part of the period during which the cement is in the 3% Na_2SO_4 solution. Thus, already after one month the calcium sulfate content of the cements attains about 22%, which is 70% of the total amount of calcium sulfate formed in six months.

The kinetics of this process and the amount of calcium sulfate formed in the cements investigated might lead one to expect that they would have identical stabilities in a sodium sulfate solution. Their stabilities in this solution vary, however, and are directly related to the rate of calcium sulfoaluminate formation in the cement and to the total amount formed. Calcium sulfoaluminate is most rapidly formed in cement V, which is richest in tricalcium aluminate. The content of calcium sulfate bound as calcium sulfoaluminate after one month in 3% Na_2SO_4 attains 10% and it reaches a maximum of 14% in two months, which corresponds to about 50% of the total amount of calcium sulfate that has accumulated in the cement. This cement (Table 6) loses 50% of its strength after only one month, and its stability coefficient SC_1 was only 0.52.

The content of calcium sulfate bound as calcium sulfoaluminate in cement VF, which has the least tricalcium aluminate content, is 7% at the end of one month, and attains a maximum of 8% after three months, which is only 27% of the total amount of calcium sulfate accumulating in the cement in six months. The strength of this cement after two months in 3% Na_2SO_4 is practically the same as that obtained in water. SC_1 and SC_2 are 0.93 and 0.91 respectively. An appreciable fall in strength occurs only in the third month: SC_3 is 0.47, and it remains at that level until the end of the six months.

Thus, in spite of accumulation of calcium sulfate in equal degree in the cements investigated, the rate of its conversion into calcium sulfoaluminate depends on the percent contents of tricalcium aluminate and tetracalcium aluminoferrite in the cements. Although the contents of silica and calcium sulfate are identical, the amount of calcium sulfoaluminate in cement V is almost double that in cement VF. It may, therefore, be considered to be established that even when there is a great accumulation of calcium sulfate in aluminoferrite cement the process of its conversion into hydrosulfoaluminate proceeds very slowly, which has a positive effect on its sulfate-stability.

The superiority of aluminoferrite cement over ordinary cement is very strikingly shown for hardening in sulfate-solutions of low magnesium content having an SO_4^{2-} content of up to 4480 mg/liter. Calcium sulfate and sulfoaluminate formation during the first month of hardening in solution No. 1, occurs at the same rate for both cements, but later—from one to six months—the picture undergoes a great change. Thus, in cement V the amount of calcium sulfate increases continuously and, at an age of six months, reaches 15%, of which 70% is in the form of sulfoaluminate; whereas in cement VF the calcium sulfate content attains 8.4% (against 7.2% at one month) including 5% of calcium sulfoaluminate, which comprises 60% of the total amount of calcium sulfate.

Thus, the hardening of cement containing 8% of tricalcium aluminate in sulfate solutions of low magnesium content is accompanied by continuous formation of calcium sulfoaluminate. In samples that have been hardened for six months the amount of sulfoaluminate attains 30%. Such a large amount of calcium sulfoaluminate is bound to lead to the disruption of the cement, which is indeed what we observe. Fall in strength begins already after two months in solution No. 1, and at six months SC_6 is 0.68.

In the aluminoferrite cement VF the process of forming calcium sulfoaluminate in a sodium sulfate solution of low magnesium content occurs only in the early period, mainly as a result of the tricalcium aluminate contained in this cement. This cement does not sustain any aggressive attack in six months in sulfate media of low magnesium content having an SO_4^{2-} content of up to 5000 mg/liter, and in pure calcium sulfate solutions it is stable at an SO_4 content of 8000 mg/liter (Table 7). According to the standards for water-aggressiveness, media for hydrotechnical concrete (GOST 4796-41) having an SO_4^{2-} content of higher than 4000 mg/liter are considered to be aggressive not only for Portland cement, but also for pozzolanic Portland cements. We may therefore consider it to be established that the aluminoferrite cement that we prepared under manufacturing conditions meets all the requirements of the standard specification mentioned for a sulfate-stable cement.

Finally, we will consider the kinetics of the accumulation of calcium sulfate and sulfoaluminate in pozzolanic Portland cements. The accumulation of calcium sulfate and sulfoaluminate in pozzolanic Portland cements having enough hydro-additive occurs only in the early part of the hardening period in the aggressive solution (3% Na_2SO_4), coming almost to a standstill in one month. After this period the total calcium sulfate content of pozzolanic cements is 10-15%, including 6-8% as calcium sulfoaluminate.

It should be noted that more sulfate accumulates in pozzolanic Portland cement containing tripolite than in pozzolanic cement containing 50% gliezh: the maximum sulfate content, 13%, is attained after a one-month hardening in 3% Na_2SO_4. As time goes on, not only does no further accumulation of calcium sulfate occur but,

on the contrary, it is even lost to some extent owing to leaching. Pozzolanic Portland cements, therefore, unlike Portland cement, should have high stability to sodium sulfate solutions, and this is actually observed. Thus, it will be seen from an examination of the results of tests on cements in 3% Na_2SO_4 that pozzolanic cements prepared from cements V and VF acquire the sulfate-stability required under technical conditions by the addition of 30% of gliezh. A pozzolanic cement prepared from cement A acquires the required sulfate-stability only when 50% of gliezh is present.

In artificially prepared solutions of low magnesium content and having an SO_4'' content of up to 5000 mg/liter the process of calcium sulfate/sulfoaluminate accumulation in pozzolanic Portland cements again occurs essentially in the early part of the hardening period. In pozzolanic cements, irrespective of the mineralogical composition of the cement clinker, the greater part of the calcium sulfate that accumulates occurs in the bound condition as calcium sulfoaluminate. The maximum amount of calcium sulfate present as sulfoaluminate is 8%, including 3% that is bound as sulfoaluminate already in the setting of the cement (because of the calcium sulfate introduced to control the setting time). Thus, owing to the interaction of free lime with sodium sulfate, only a further 5% of bound $CaSO_4$ is formed (as sulfoaluminate). Such an amount of calcium sulfoaluminate in pozzolanic Portland cement cannot have a deleterious effect on the stability of salt solutions of low magnesium content. Hence, all of the pozzolanic cements studied, not only with 50%, but also with 30% of gliezh, harden in salt solutions of low magnesium content (close in composition to the subsoil waters of a number of Central Asian districts) in the same way as in water.

The main results of the investigations may be summarized as follows:

1. A cement containing up to 5% of tricalcium aluminate and a total content of mineral fluxes of up to 22% even with a saturation coefficient of 0.92, is stable in sulfate solutions of low magnesium content (containing up to 3000 mg/liter of magnesium sulfate) and having an SO_4'' content of up to 5000 mg/liter. The formation of calcium sulfate and sulfoaluminate occurs only in the early part of the hardening period and practically ceases by the end of one month.

2. Addition of gliezh to cement of low tricalcium aluminate content (up to 5%) has an exceptionally favorable effect on its sulfate-stability. Its favorable effect is already appreciable when a 15% amount of gliezh is added. Such a cement, containing 15% of gliezh, is not attacked in sulfate solutions of low magnesium content having an SO_4'' content of up to 7000 mg/liter.

3. A pozzolanic cement containing 30% of gliezh, prepared from a Portland cement having a tricalcium aluminate content of up to 8% and a total content of mineral fluxes of up to 20%, hardens in sulfate solutions close in composition to the aggressive subsoil waters of Central Asia in the same way as in fresh water.

4. Pozzolanic cement containing 50% of gliezh and prepared from a Portland cement having a tricalcium aluminate content of up to 5% and a total content of mineral fluxes of up to 21% with a saturation coefficient of 0.80-0.92 is stable in 3% solution of sodium sulfate: the stability coefficient, SC_6, is not less than 0.80. Formation of calcium sulfate and sulfoaluminate is to be observed only in the early part of the hardening period (up to one month). As time goes on this process dies down.

In this way we have shown that it is possible to manufacture in one of the cement works of the Republic a whole series of special cements that satisfy the requirements of the constructors of the Main Turkmen Canal for use in different zones of the canal.

Local loess-like clayey soils are of considerable interest for the preparation of hydrotechnical cements in the Central Asian Republics. We have shown [11] that these loess-like soils, when roasted in the range 650-750° acquire the properties of hydraulic binding materials. The hydraulic binding properties are caused by the formation, during the roasting, of calcium monoaluminate and β-orthosilicate. The cement so obtained is called "loess cement". The hardening of this cement proceeds with formation of a hydrogel of calcium monosilicate and dicalcium hydroaluminate. It is considerably better in strength than the best types of Roman cement. Loess cement hardens better in sulfate solutions than in fresh water. The low stability of loess cement to the atmosphere, which is the result of the deleterious action of atmospheric carbon dioxide, is completely eliminated by additions of silicate cement.

As a result of laboratory and factory (pilot and full-scale) investigations [12], it has been found possible to prepare loess cements of three grades, varying in mechanical strength:

1. Grade "250", with 50% of Portland cement
2. Grade "200", with 30% of Portland cement
3. Grade "100", with 10% of Portland cement

Cements of grades "200" and "250" may be used in the same way as pozzolanic cements in concrete and ferroconcrete for hydrotechnical construction, the loess cement with 10% of Portland cement being for mortars. Loess cement with 50% of Portland cement has been approved for hydrotechnical construction and is to be recommended as a high-quality hydrotechnical cement.

Among the important questions of cement chemistry and technology that have not yet been solved and yet are of great practical significance is the question of the aggressive action of magnesium-containing waters. In sulfate solutions of low magnesium content, (up to 1% magnesium sulfate) sulfate-stable pozzolanic cements do not suffer aggressive attack, but in solutions of higher concentration they are broken down even more rapidly than Portland cements. The question of the preparation of cements stable to magnesium sulfate solutions of high concentration is therefore a very vital one.

In view of this, an investigation of a senior scientist of our laboratory, Ragozina, is of great interest. In a study of the hardening processes in salt solutions of synthetic cements consisting of various proportions of calcium monoaluminate and calcium orthosilicate, Ragozina showed that they are extremely resistant to the aggressive action of sulfate- and magnesium-containing waters. Pursuing these investigations, Ragozina obtained a siliceous belite cement. This cement in admixture with 15% of anhydrite, which has a strength in plastic mortars of 200 kg/sq. cm., has a high degree of stability in a 3% solution of magnesium sulfate.

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*NKPS = Peoples Commissariat of Railroads.

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OPTICALLY ACTIVE ORGANOMERCURY COMPOUNDS

COMMUNICATION 1. PREPARATION OF THE DIASTEREOISOMERIC (l) MENTHYL ESTERS OF (BROMOMERCURI)PHENYLACETIC ACID

A. N. Nesmeyanov, O. A. Reutov, and S. S. Poddubnaya

Optically active organometallic compounds containing a metal atom linked to an asymmetric carbon atom have received very little study. Only investigations on the preparation of optically active organometallic compounds of alkali metals, magnesium, and mercury have appeared in the literature. In spite of numerous attempts [1-7] optically active organometallic compounds of the alkali metals have only recently been prepared. Letsinger [8] in 1950, was successful in preparing 1-methylheptyllithium, the optical activity of which he inferred from an examination of its carbonation product.

Attempts to prepare optically active organomagnesium compounds have not been successful [9-11]. the work of Whitmore and Harriman [12] on the preparation of an optically active organomagnesium compound from 1-bromo-2-methylbutane in which the magnesium was attached to the carbon atom adjacent to the asymmetric carbon must be regarded with some doubt, as the experimental results are not sufficiently decisive.

Optically active organomercury compounds have been prepared by Marvel and coworkers by the addition of mercuric acetate to the menthyl [13] and bornyl [14] esters of cinnamic acid:

$$C_6H_5{-}CH{=}CH{-}COOR + Hg(CH_3COO)_2 + CH_3OH \rightarrow C_6H_5{-}\underset{OCH_3}{\overset{\bullet}{C}}H{-}\underset{HgOCOCH_3}{\overset{\bullet}{C}}H{-}COOR + CH_3COOR.$$

The acetate was converted into the chloride, bromide, or iodide by the action of potassium chloride, bromide, or iodide, and then separation of the diastereoisomers was carried out. In all cases only two diastereoisomers were obtained instead of the four that are theoretically possible, a circumstance that led Pfeiffer [15] to doubt the correctness of the formulas given above for the products of the addition of mercuric acetate to cinnamic esters and to suggest that these addition products are complex compounds. In view of the results of one of us with coworkers [16-19] concerning the structure of the products of addition of heavy-metal halides to acetylene and ethylene and the causes of their dual reactivity, it can now scarcely be doubted that the products of addition of mercuric acetate to cinnamic esters are true organometallic compounds.

In this connection, two suppositions are possible. First, we may suppose that Sandborn and Marvel failed to separate all of the four diastereoisomers. Second, we may suppose that in the addition of mercuric acetate to cinnamic esters only two of the four possible diastereoisomers are actually formed owing to the existence of stereochemically directed addition of mercury salts at a carbon-carbon double bond (trans addition).

We decided to prepare an optically active organomercury compound having a structure that would permit the possibility of existence of only two diastereoisomers, and for this purpose we applied the reaction of bromo derivatives with mercury* devised by two of us in conjunction with Besprozvanny [20]. (l) menthyl bromo(phenyl) acetate reacted on being shaken vigorously with mercury, yielding an optically active organomercury compound.

$$C_6H_5{-}\underset{Br}{\overset{\bullet}{C}}H{-}COOC_{10}H_{19} + Hg \rightarrow C_6H_5{-}\underset{HgBr}{\overset{\bullet}{C}}H{-}COOC_{10}H_{19}$$

We carried out this reaction for the two stereoisomeric menthyl esters of bromo(phenyl)acetic acid. The following constants are given in the literature [21] for the two stereoisomers: stereoisomer I - m.p. 78-79°, $[\alpha]_D$ +9.4°; stereoisomer II - m.p. 40-41°, $[\alpha]_D$ - 139.8°. The constants that we obtained for isomer I agreed with the figures in the literature, but, in spite of the fact that we performed the synthesis of menthyl bromo(phenyl)acetate

* Other methods for the synthesis of organomercury compounds (with the aid of the Grignard reagent, by the action of sodium amalgam on halogen derivatives, etc.), are not applicable here because they do not permit the preparation of organomercury compounds containing active groups, without which it is not possible to separate the stereoisomers.

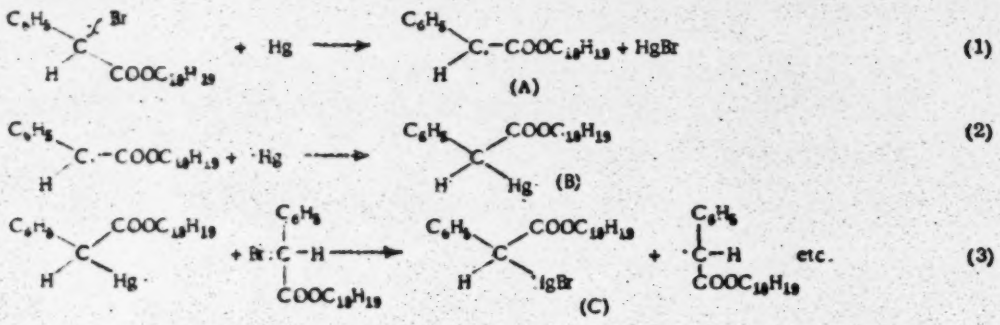
or less than fifteen times by two different routes, we never succeeded in obtaining isomer II in a crystalline form, either by allowing the substance to stand for a long period (two months), nor by attempting to recrystallize it from various solvents. The specific rotation of the isomer II that we obtained was $[\alpha]_D^{18} = -96.5°$.

The two stereoisomers reacted with mercury at different rates. Thus, the reaction of isomer II with excess of mercury proceeded in the cold under vigorous shaking for 30-60 minutes, giving 29% of the theoretical yield. The solid isomer I, however, when shaken in benzene solution with mercury in the cold for 250 hours gave only a 2.4% yield of organomercury compound. This very slow reaction is evidently associated with the reduction in the concentration of the menthyl ester. Apart from this, the best solvent for the reactions of halogen derivatives of aliphatic or acyl substituted aliphatic compounds with mercury is generally ethanol (and not benzene), which cannot be used in the present case owing to the poor alcohol-solubility of the solid menthyl ester. The differing rates of reaction must depend, of course, to some extent on the fact that the two isomers are not enantiomorphs, but diastereoisomers, and therefore will in general have differing reactivities. If the reaction of the solid isomer of menthyl bromo(phenyl)acetate with mercury is carried out at 95-100° without solvent, reaction is complete in four hours and leads to the formation of the organomercury compound in 36% yield.

When mercury reacted with either the liquid or the solid isomer of menthyl bromo(phenyl)acetate, a mixture of two diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid was formed. The organomercury diastereoisomers were separated by fractional crystallization from methanol or acetone. The constants of the compounds obtained were: diastereoisomer I - m.p. 162-163°, $[\alpha]_D^{18} - 96.5° \pm 1°$; diastereoisomer II - m.p. 152-154°, $[\alpha]_D^{18} - 49.3° \pm 1°$.

It must be noted that when either the liquid* or the solid isomer of menthyl bromo(phenyl)acetate reacts with mercury an equimolecular mixture of organomercury diastereoisomers is formed (angles of rotation of the mixtures of diastereoisomers formed in various cases were −71.1°, −73.8° and −75.7°, and the calculated angle of rotation of an equimolecular mixture of diastereoisomers is $(-\frac{96.5 + 49.3}{2} = -72.9° \pm 1°)$. This fact indicates that a free radical with an odd electron on carbon does not preserve the configuration of the compound from which it is formed, but becomes flat.**

As has been shown [20], the reaction of mercury with alkyl halide is homolytic, and is accelerated by addition of organic peroxides and by exposure to ultraviolet radiation. Thus, the reaction of menthyl bromo(phenyl)acetate (whether it be isomer I or isomer II) with mercury may be represented as follows:



(1)

(2)

(3)

The first stage consists in homolytic rupture of the C−Br bond owing to the attack of a mercury atom (or under the action of light) with formation of a free radical.

If the unpaired electron of the free radical were able to maintain the configuration, then one of the organomercury diastereoisomers would form, if not the sole, then the predominating product. Since it is found in practice that each of the isomeric menthyl bromo(phenyl)acetates forms an equimolecular mixture of organomercury diastereoisomers, it is obvious that the radical A has a flat configuration, as a result of which the attack on it by a mercury atom may occur, with equal probability, from either side.

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* The fact that the liquid isomer of menthyl bromo(phenyl)acetate may have contained some of its diastereoisomer is of no significance in our method of working.

** Contradictory hypotheses on this matter appear in the literature: thus, Wallis, and Adams [22] and also Brown, Kharasch, and Chao [23] consider that a free radical has a flat configuration, whereas Karagunis and Drikos [24] consider that the odd electron of the free radical is able to maintain the configuration.

EXPERIMENTAL

1. Preparation of the Diastereoisomeric (l)-Menthyl Esters of Bromo(phenyl)acetic Acid.

The menthyl ester of racemic bromo(phenyl)acetic acid was obtained in 68.5 % yield by the esterification of bromo(phenyl)acetic acid with (l)-menthol in presence of hydrogen chloride [21]. On standing, the substance partly crystallized out. After one week the precipitate was filtered off and recrystallized twice from methanol: m.p. 80°; $[\alpha]_D^{18}$ + 10.9° ± 0.3° (in alcohol) (C = 2.333•; l = 2; α_D^{18} + 0.66° ±0.02°). data in the literature: 78-79°; $[\alpha]_D$ + 9.4° (in alcohol) [21].

Found %: C 61.30; 61.32; H 7.24; 7.28
$C_{18}H_{25}O_2Br$. Calculated %: C 61.19; H 7.13

The isomer D was obtained in the form of a thick liquid. The substance did not crystallize out when allowed to stand for two months; it did not crystallize also from aqueous alcohol, heptane, benzene, ether, and other solvents: b.p. 223-225°/22 mm; $[\alpha]_D^{18}$ −98.5° (in alcohol). (C = 0.739; l = 2, α_D^{18} −1.13°). Data in the literature: 40-41°; $[\alpha]_D^{18}$ −139.8° [21]. 225°/22 mm [25].

2. Reaction of the (l)-Menthyl Esters of (d)- and (l)-Bromo(phenyl)acetic Acids with Mercury.

a) Reaction of the liquid isomer of (l)-menthyl bromo(phenyl)-acetate with mercury. A mixture of 149 g (0.42 mole) of the (l) menthyl ester of bromo(phenyl)acetic acid having $[\alpha]_D^{18}$ −98.5° and 1177 g (5.86 g-atom) of mercury was shaken vigorously until it thickened (30 minutes). A day later the thick reaction mixture was washed with 90% alcohol, and the organomercury compound was extracted from the residue with acetone. After evaporation of the acetone, crude (l)-menthyl (bromomercuri)phenylacetate (68 g, 29.2%) was obtained. The angle of rotation of the uncrystallized substance (washed with cyclopentane) was: $[\alpha]_D^{18}$ −71.1° •• (C = 0.777; l = 2; α_D^{18} −0.96°). After recrystallization from alcohol it had an m.p. 158-161°, $[\alpha]_D^{18}$ −74.6° (C= 2.037; l = 2, α_D^{18} −2.67°).

Found %: C 39.02; 39.14; H 4.59; 4.55
$C_{18}H_{25}O_2HgBr$. Calculated %: C 39.03; H 4.55

The (l)-menthyl (bromomercuri)phenylacetate obtained dissolved readily in chloroform and acetone, not so readily in benzene and toluene, and poorly in ether. It could be crystallized from ethanol, methanol, carbon tetrachloride, benzene, and acetone. The substance is here described for the first time.

After recrystallization from various solvents, the substance gave various values of specific rotation. Thus, from acetone: $[\alpha]_D^{18}$ −91.2° (C = 0.731; l = 2; α_D^{18} −1.17°); from carbon tetrachloride: $[\alpha]_D^{18}$ −64° (C = 0.95; l = 2, α_D^{18} −1.07°); and from benzene: $[\alpha]_D^{18}$ −75.2° (C = 0.643; l = 2, α_D^{18} −0.85°).

The great extent to which the angle of rotation depends on the nature of the solvent from which the substance is crystallized gives us reason to suppose that the substance is a mixture of two diastereoisomers of differing solubility and rotatory power.

b) Reaction of the solid isomer of (l)-menthyl bromo(phenyl)-acetate with mercury in benzene. A mixture of 35 g (0.09 mole) of the menthyl ester of bromo(phenyl)acetic acid having m.p. 80° and specific rotation $[\alpha]_D^{18}$ +10.9° dissolved in benzene, and 88 g (0.44 g-atom) of mercury was shaken for about 250 hours. The benzene was evaporated off, and the residue was washed with alcohol and extracted with hot acetone. The organomercury compound and unchanged menthyl bromo(phenyl)acetate went into the acetone. The acetone was evaporated off and the organomercury compound was washed free of starting material by means of ether. The product was menthyl (bromomercuri)phenylacetate (1.3 g, 2.4 %) of m.p. 155-156°. After recrystallization from methanol it melted at 157-158°. A mixed melting point with authentic menthyl (bromomercuri)phenylacetate (m.p. 157-158°; $[\alpha]_D^{18}$ −75.8°) showed no depression. The specific rotation was $[\alpha]_D^{18}$ − 73.8° (C = 0.783; l = 2; α_D^{18} −1.02°).

c) Reaction of the solid isomer of the menthyl ester of bromo(phenyl)acetic acid with mercury at 95-100°. A mixture of 79 g (0.22 mole) of the menthyl ester of bromo(phenyl)acetic acid (m.p. 79-80°; $[\alpha]_D^{18}$ + 11.2°) and 235 g (0.86 g-atom) of mercury was heated for four hours at 95-100° with vigorous shaking. Toward the end of this period the original liquid reaction mixture began to become solid. After one day the mixture was washed with

• The concentration C is always expressed in grams of substance per 100 g of solvent.

•• Here and elsewhere the specific rotation is measured in benzene.

ether to remove unchanged starting material and the organomercury compound formed was extracted with chloroform. Evaporation of the chloroform yielded a residue of menthyl (bromomercuri)phenylacetate (44.5 g, 35.9%), which melted, after being recrystallized from methanol, at 155-157°. It had $[\alpha]_D^{20}$ −75.7° (C = 0.764, l = 2; α_D^{20} −1.02°).

Separation of the Diastereoisomeric (l) Menthyl Esters of (d)- and (l)-(Bromomercuri)phenylacetic Acids.

The separation of these substances was carried out by repeated recrystallization. Attempts to use benzene and carbon tetrachloride as solvents were not successful. After the substance had been recrystallized three times from benzene, it became dark in color owing to partial decomposition with separation of mercury. When it was recrystallized from carbon tetrachloride, its angle of rotation changed to an inappreciable extent. Thus after three recrystallizations $[\alpha]_D^{20}$ was −73.1°, and after four it was −78.5°. For complete separation of the diastereoisomers, several more recrystallizations would have been necessary.

It was found possible to effect the complete separation of the diastereoisomers by recrystallization from a large amount of methanol (6 g of menthyl [bromomercuri]phenylacetate from 200 ml of methanol). The first recrystallization yielded a substance of m.p. 159-160° and $[\alpha]_D^{20}$ −89.7° (C = 0.656, l = 2; α_D^{20} −1.03°). A second recrystallization yielded 2.5 g of substance of m.p. 162-163° and $[\alpha]_D^{20}$ −96.7° (C = 0.658; l = 2; α_D^{20} −1.12°).

Further recrystallization produced no further change in angle of rotation and melting point. Thus, after the third recrystallization the substance had an m.p. 162-163° and $[\alpha]_D^{20}$ −96.4° ± 1° (C = 0.635; l = 2; α_D^{20} −1.10° ± ± 0.01°). The substance is described for the first time.

	Found %	C 39.18, 39.19; H 4.55, 4.74
$C_{16}H_{23}O_2HgBr$	Calculated %	C 39.03 H 4.78

The readily soluble isomer B of the menthyl ester of (bromomercuri)phenylacetic acid was separated from the filtrate from the first crystallization, which was evaporated to dryness. The residue was fractionally crystallized from methanol. For this purpose it was dissolved in the least possible amount of boiling methanol, and when the solution was cooled a precipitate formed (Fraction I) of m.p. 159-160° and $[\alpha]_D^{20}$ −85.5° (C = 0.666, l = 2; α_D^{20} −1.00°). Each of the following fractions was a precipitate formed by evaporation of the filtrate to half volume. The angle of rotation of Fraction III was $[\alpha]_D^{20}$ −82.5° (C = 0.703, l = 2, α_D^{20} −0.65°); and that of Fraction IV, $[\alpha]_D^{20}$ −80.9° ± 1 (C = 0.483, l = 2, α_D^{20} −0.43° ± 0.01°). There was no further change in the angle of rotation; thus Fraction V had $[\alpha]_D^{20}$ −49.3° ± 1° (C = 0.671; l = 2; α_D^{20} −0.57° ± 0.01°), m.p. 152-154°. The substance is described for the first time.

	Found %	C 39.31, 39.35; H 4.75, 4.74
$C_{16}H_{23}O_2HgBr$	Calculated %	C 39.03, H 4.55

The separation of the diastereoisomers can be effected also by recrystallization from acetone. After two recrystallizations from acetone a substance was obtained having m.p. 160-161° and $[\alpha]_D^{20}$ −92.4° (C = 0.695; l = 2; α_D^{20} −1.13°). After three recrystallizations from acetone the substance had an m.p. 162-163° and $[\alpha]_D^{20}$ − 95.9 ± ± 1° (C = 0.725; l = 2, α_D^{20} −1.36° ± 0.01°).

SUMMARY

1. When the stereoisomeric (l)-menthyl esters of bromo(phenyl)acetic acid react with mercury, an equimolecular mixture of diastereoisomeric menthyl esters of (bromomercuri)phenylacetic acid is formed in each case.

2. The fact of the formation of an equimolecular mixture of the diastereoisomers of (l)-menthyl (bromomercuri)phenylacetate is an argument in favor of the hypothesis that a free radical having an unpaired electron on a carbon atom has a plane configuration.

3. The two diastereoisomers of the (l)-menthyl ester of (bromomercuri)phenylacetic acid have been obtained in a pure state by fractional crystallization of their mixture from methanol or acetone.

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SYNTHESIS OF ORGANOMERCURY COMPOUNDS BY REACTION OF ORGANIC HALOGEN COMPOUNDS WITH MERCURY

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In the literature a few examples have been described of reactions of organic iodine compounds with mercury in which organomercury compounds are formed. These include the reactions of methyl iodide [1], ethyl iodide [2], allyl iodide [3], propargyl iodide [4], iodo(phenyl)acetylene [5], diiodomethane, iodoform [6], and benzyl iodide [7] with mercury. It has been considered that chlorine and bromine compounds of the aliphatic and aryl substituted aliphatic series (with the exception of bromobenzyl cyanide [8]), and also all aryl halides, do not react with mercury.

In the present and previous [9] papers it is shown that bromine compounds in which the carbon-bromine bond is activated by conjugation with a double bond ($>C=C-C-Br$ or $O=C-C-Br$), are able to react with mercury to give organomercury compounds of the type R–HgBr; aromatic iodine derivatives are able to react with mercury to give organomercury compounds only in presence of ultraviolet radiation.

Allyl bromide reacted slowly with mercury in the dark, forming allylmercury bromide:

$$CH_2=CH-CH_2Br + Hg \longrightarrow CH_2=CH-CH_2HgBr.$$

It was found that the reaction is accelerated by irradiation of the reaction mixture by means of a quartz mercury lamp contained in a glass vessel, and is further accelerated when the glass vessel is replaced by a quartz one, which transmits ultraviolet rays; in the latter case, vigorous stirring* is necessary, since otherwise organomercury polymers form rapidly on the walls of the quartz vessel. The results obtained for reactions of allyl bromide with excess of mercury under various conditions are given in Table 1.

Cinnamyl bromide reacted rapidly with mercury without irradiation, forming cinnamylmercury bromide in 82% yield:

$$C_6H_5-CH=CH-CH_2Br + Hg \longrightarrow C_6H_5-CH=CH-CH_2-HgBr.$$

This reaction goes so vigorously that the cinnamyl bromide must be diluted with ethanol in order to obviate its polymerization and resinification.

Ethyl bromo(phenyl)acetate readily reacted with mercury without irradiation, giving ethyl (bromomercuri)-phenylacetate in 73% yield:

$$C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-COOC_2H_5 + Hg \longrightarrow C_6H_5-\underset{\displaystyle HgBr}{\underset{|}{CH}}-COOC_2H_5$$

The (l)-menthyl ester of bromo(phenyl)acetic acid reacted in like manner.

We considered it to be of interest to study some of the properties of the representatives that we had prepared of this previously undescribed class of α-mercurated esters. When treated with dry ammonia in chloroform solution, the ethyl and (l)-menthyl esters of (bromomercuri)phenylacetic acid symmetrized in accordance with the equation:

$$2\,C_6H_5-\underset{\displaystyle HgBr}{\underset{|}{CH}}-COOR + 2NH_3 \longrightarrow ROOC-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-Hg-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-COOR + NH_2HgBr + NH_4Br.$$

We studied also the reaction of a (bromomercuri)phenylacetic ester with acetyl chloride in a medium of dry

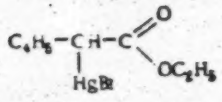
* We found the most suitable stirrer to be a rapidly rotating bottle brush. An improvised stirrer of this type produces a good emulsion of the mercury in the halogen compound and constantly removes the film of solid reaction products that forms on the wall of the test tube and would otherwise impede irradiation of the reaction mixture.

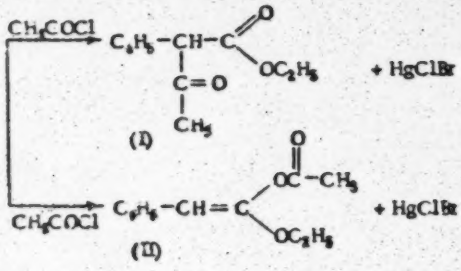
TABLE 1

Reaction of Allyl Bromide with Mercury

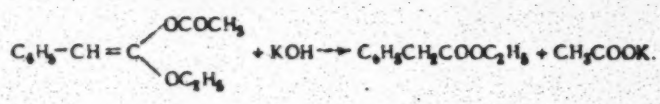
No.	Source of irradiation	Reaction vessel	Agitation	Amt. of allyl bromide(g)	Duration of reaction (hr)	Yield (%)	Notes
1	Lamp PRK-4	Quartz test tube	Vibratory machine	10	48	9	Apart from $CH_2=CHCH_2HgBr$, 1.5 times as much organomercury polymer was formed.
2	Lamp PRK-4	Glass test tube	Vibratory machine	11	48	20	Forms pure allylmercury bromide without appreciable contamination with polymeric compounds.
3	"	Quartz test tube	Stirrer	11.7	19	30	"
4	"	Glass test tube	"	14.8	28	4	"
5	Not irradiated (in the dark)	"	Vibratory machine	5.2	48	Less than 1	"
6	"	"	"	5.2	120	5	"
7	"	"	"	5.2	600	32	"

toluene. Heating of the reaction mixture on a water bath resulted in elimination of mercuric halide and formation of two products: the C-acetyl(phenyl)acetic ester I and the acetate of the enol form of phenylacetic ester (II).





Formation of the substance (II) was shown by the fact that phenylacetic ester and acetic acid are formed by treatment of the mixture of (I) and (II) with a 2.5% aqueous solution of caustic potash in the cold:



Thus in contrast with α-mercurated aldehydes and ketones, which react with acid chlorides with exclusive formation of vinyl esters [10, 11], for example:

$$ClHgCH_2CHO + CH_3COCl \rightarrow CH_2=CH-OCOCH_3 + HgCl_2,$$

the (bromomercuri)phenylacetic ester reacted with acetyl chloride with formation of both an O-derivative (with transfer of the reactive center) and a C-derivative (without transfer of the reactive center).

An attempt to prepare the simplest α-mercurated ester from ethyl bromoacetate was not successful. When the reaction mixture was exposed to ultraviolet radiation, only very small amounts of mercurous and mercuric bromides were formed.

On the other hand, ethyl iodoacetate reacted with mercury when irradiated, giving ethyl iodomercuriacetate, although in low yield:

$$I-CH_2COOC_2H_5 + Hg \xrightarrow{h\nu} I-Hg-CH_2-COOC_2H_5.$$

Even aromatic iodine derivatives reacted with mercury when exposed to ultraviolet radiation, giving the corresponding organomercury compounds •, for example,

$$C_6H_5I + Hg \xrightarrow{h\nu} C_6H_5HgI; \qquad \alpha\text{-}C_{10}H_7I + Hg \xrightarrow{h\nu} \alpha\text{-}C_{10}H_7HgI.$$

When mercury reacted with polybromo- and polychloro-methanes, no organomercury compounds were formed. Bromoform reacted slowly with mercury, even without irradiation, the reaction being appreciably accelerated in presence of benzoyl peroxide or by exposure to ultraviolet radiation. Formation then occurred of a mixture of mercurous and mercuric bromides, and also of small amounts of pentabromoethane as a result of secondary processes.

Boiling carbon tetrachloride did not react to an appreciable extent with mercury. The reaction went slowly in the presence of ultraviolet radiation at room temperature, and more rapidly at the boiling point of carbon tetrachloride in the presence of benzoyl peroxide, or when a mixture of carbon tetrachloride with mercury applied on barium sulfate was heated in a sealed tube at 120-130°:

$$2CCl_4 + 2Hg \longrightarrow CCl_3-CCl_3 + Hg_2Cl_2.$$

Chloroform, like carbon tetrachloride, reacted very slowly with mercury when irradiated without being heated; it formed calomel. Other cases that we have studied of the reactions of halogen compounds with mercury are given in Table 2.

Formation of organomercury compounds probably proceeds as a result of homolytic reaction, which may be represented as follows:

$$\left.\begin{array}{l} R{:}X \xrightarrow{h\nu} R\cdot + \cdot X \\ \text{or} \quad R{:}X + \cdot Hg\cdot \longrightarrow R\cdot + \cdot HgX \end{array}\right\} \qquad (I)$$

$$R\cdot + \cdot Hg\cdot \longrightarrow R-Hg\cdot \qquad (II)$$

$$R-Hg\cdot + X{:}R \longrightarrow R-HgX + \cdot R \qquad (III)$$

According to the nature of the radical and of the halogen, various side reactions may occur in varying degree (dimerization of the radicals, their reaction with molecules of halogen derivative, etc.).

EXPERIMENTAL ••

1. Reaction of Allyl Bromide with Mercury

a) A mechanically shaken mixture of allyl bromide (10 g) and mercury (34 g: a two-fold excess), contained in a quartz test tube, was exposed for 48 hours to ultraviolet radiation.••• From the reaction mixture, which had become thick, unchanged allyl bromide was distilled off, and the residue was extracted with acetone. After evaporation of the acetone, the dry residue was extracted with alcohol, yielding allylmercury bromide (2.4 g, 9%). The alcohol-insoluble residue had a low indefinite melting point and was evidently a polymer of allylmercury bromide. Allylmercury bromide dissolves readily in acetone, dioxane, and allyl bromide, poorly in ether, and is insoluble in petroleum ether. Melting point (from aqueous alcohol) 116-118° (when heated rapidly). When the capillary is heated slowly, the substance is converted into an infusible polymer. Analysis for mercury gave somewhat high results, for, on being heated with hydrochloric acid, the substance was partially carbonized.

	Found %:	C 11.26; 11.08; H 1.70; 1.78
C_3H_5HgBr.	Calculated %:	C 11.18 H 1.55

The literature [12] gives m.p. 124-125°.

b) A mechanically shaken mixture of allyl bromide (11 g) and mercury (36 g; a two-fold excess) was irradiated in a glass test tube for 48 hours. The reaction mixture, treated as in the previous experiment, yielded 6.3 g (20%) of allylmercury bromide. No appreciable amounts of polymeric organomercury compounds were formed in this or the three following experiments.

• Almost simultaneously with us [9], Razuvaev and Shubenko [17] effected the synthesis of phenylmercury iodide from iodobenzene and mercury in the presence of radiation.

•• The students M. A. Besprozvanny and S. S. Poddubnaya assisted in the performance of the experiments.

••• In all cases irradiation was carried out with the aid of a quartz mercury lamp PRK-4, the tube of which was placed at 20 cm from the reaction vessel.

c) A mixture of allyl bromide (11.7 g) and mercury (60 g: a three fold excess) was irradiated for 19 hours while being stirred in a quartz test tube provided with a reflux condenser and a stirrer made from a bottle brush. When reaction was complete, the usual treatment yielded 9.3 g (30%) of allylmercury bromide.

TABLE 2

Reaction of Organic Halogen Derivatives with Mercury

Original halogen derivative		Reaction conditions	Organomercury compound formed	Yield (%)	Other reaction products
Name	Formula				
Allyl bromide	$CH_2=CHCH_2Br$	Not irradiated, room temperature	$CH_2=CHCH_2HgBr$	32	None
Allyl chloride	$CH_2=CHCH_2Cl$	Irradiated, 40°	None	–	Hg_2Cl_2
Cinnamyl bromide	$C_6H_5CH=CHCH_2Br$	Not irradiated, room temperature	$C_6H_5CH=CHCH_2HgBr$	82	None
Cinnamyl chloride	$C_6H_5CH=CHCH_2Cl$		None	–	None
		Irradiated, 40°	None	–	Hg_2Cl_2, polymerization products of original substance.
Benzyl bromide	$C_6H_5CH_2Br$	a) Not irradiated, room temp.	None	–	None
		b) Not irradiated, 80°	None	–	Hg_2Br_2, $HgBr_2$, HBr, resin
		c) Irradiated, room temp.	None	–	Hg_2Br_2, $HgBr_2$, HBr, resin
(2 Bromoethyl)benzene	$C_6H_5CHBrCH_3$	Irradiated, 40°	None	–	Hg_2Br_2, HBr, resin
Ethyl 2 bromopropionate	$CH_3CHCOOC_2H_5$ (Br)	Irradiated, 40°	None	–	Hg_2Br_2
Ethyl 2 bromobutyrate	$CH_3CH_2CHCOOC_2H_5$ (Br)	Irradiated, 40°	None	–	Hg_2Br_2
Diethyl bromomalonate	$CHBr(COOC_2H_5)_2$	Irradiated, 40°	Organomercury polymer	–	None
Ethyl 2 bromo acetoacetate	$CH_3COCHCOOC_2H_5$ (Br)	Not irradiated, room temperature	Organomercury polymer	–	None
Ethyl bromo(phenyl)acetate	$C_6H_5CHCOOC_2H_5$ (Br)	Not irradiated, room temperature	$C_6H_5CHCOOC_2H_5$ (HgBr)	73	None
(l) Menthyl bromo(phenyl)acetate	$C_6H_5CHCOOC_{10}H_{19}$ (Br)	Not irradiated, room temperature	$C_6H_5CHCOOC_{10}H_{19}$ (HgBr)	31	None
Ethyl bromo(phenyl)p tolylacetate	C_6H_5, $CBrCOOC_2H_5$, $CH_3C_6H_4$	Not irradiated, room temperature	None	–	None
Ethyl 2 bromo 2 phenylpropionate	CH_3, $C_6H_5CBrCOOC_2H_5$	Not irradiated, room temperature	None	–	None
Ethyl bromoacetate	$BrCH_2COOC_2H_5$	Irradiated, 40°	None	–	Hg_2Br_2, $HgBr_2$
Ethyl iodoacetate	$ICH_2COOC_2H_5$	Irradiated, 40°	$IHgCH_2COOC_2H_5$	–	Hg_2I_2, HgI_2
2 Bromopropionaldehyde	$CH_3CHBrCHO$	Irradiated, 40°	None	–	Hg_2Br_2, $HgBr_2$

TABLE 2 — (continued)

Original halogen derivative		Reaction conditions	Organomercury compound formed	Yield (%)	Other reaction products
Name	Formula				
Bromo(phenyl)-acetaldehyde	$C_6H_5CHBrCHO$	Not irradiated, room temperature	Organomercury polymer	—	None
Bromomethyl phenyl ketone	$C_6H_5COCH_2Br$	Irradiated, 60°	None	—	None
Bromoform	$CHBr_3$	a) Not irradiated, 100°	None	—	Hg_2Br_2, $HgBr_2$, CBr_3-CHBr_2
		b) Irradiated, 40°	None	—	Ditto
Chloroform	$CHCl_3$	Irradiated, 40°	None	—	Hg_2Cl_2
Carbon tetrachloride	CCl_4	a) Boiling in presence of benzoyl peroxide	None	—	Ditto
		b) Heating in sealed tubes (120-130°)	None	—	Ditto
Iodobenzene	C_6H_5I	Irradiated, 40°	C_6H_5HgI	8	Hg_2I_2
1-Iodonaphthalene	α-$C_{10}H_7I$	Irradiated, 40°	α-$C_{10}H_7HgI$	6-8	Hg_2I_2

d) A mixture of allyl bromide (14.8 g) and mercury (47 g: a two-fold excess) was irradiated for 28 hours while being stirred in a glass test tube provided with a reflux condenser and a stirrer made from a bottle brush. The usual treatment yielded 1.5 g (4%) of allylmercury bromide.

e) A mixture of allyl bromide (5.2 g) and mercury (22 g: 150% excess) was shaken for 600 hours in a test tube wrapped in black paper. The usual treatment yielded 4.5 g (32%) of allylmercury bromide. When this experiment was carried out for 120 hours, allylmercury bromide was formed in 5% yield, and when it was carried out for 48 hours, the yield of organomercury compound was less than 1%.

2. Reaction of Cinnamyl Bromide with Mercury

Cinnamyl bromide (19.7 g = 0.1 mole) was mixed with an equal volume of 96% ethanol and with 100.3 g (0.5 g-atom) of mercury. After being shaken vigorously for 15 minutes the reaction mixture became slightly warm and thickened. Unchanged mercury was poured off, and ethanol was added to the mixture until a slurry was formed. The precipitate was filtered off, and the organomercury compound was extracted from it with benzene. The benzene solution was evaporated until crystallization began, and when crystallization was complete (2-3 hours) the cinnamylmercury bromide was filtered off under suction and washed with cold benzene; the yield was 32.7 g (82%). The substance was obtained in the form of creamy white scales, readily soluble in cold acetone, hot benzene, hot methanol, and hot ethanol, poorly soluble in cold benzene, cold methanol, and cold ethanol. Benzene was found to be the most satisfactory solvent for crystallization purposes; when crystallization was carried out from methanol or ethanol, the substance underwent appreciable decomposition with separation of mercury and formation of polymeric products. When heated quickly, the substance melted at 340-345°, but when heated slowly in the capillary it polymerized without melting. This substance is described for the first time.

Found %: C 27.33; 27.15; H 2.41; 2.49
C_9H_9HgBr. Calculated %: C 27.18; H 2.28

Found %: Hg 50.42, 50.34
C_9H_9HgBr. Calculated %: Hg 50.45

3. Reaction of Ethyl Bromo(phenyl)acetate with Mercury

A mixture of 150 g (0.617 mole) of ethyl bromo(phenyl)acetate and 480 g (2.38 g-atoms) was shaken for 30 minutes in a flask having a ground-in stopper. When the mixture had set solid, it was allowed to stand for 2-3 hours. The organomercury compound was extracted with boiling chloroform. The crystals obtained after evaporation of the chloroform were washed with a small amount of carbon tetrachloride to remove unchanged ethyl bromo(phenyl)acetate

...d then crystallized from ethanol. The yield was 200 g (73%), m.p. 125-126°. Ethyl (bromomercuri)phenylacetate is readily soluble in chloroform, hot acetone, and hot ethanol, not so soluble in benzene, cold ethanol, and carbon tetrachloride, insoluble in petroleum ether. It is readily decomposed by concentrated hydrochloric acid with formation of ethyl phenylacetate and mercuric chloride. The substance is described for the first time.

Found %: Hg 45.42; 45.72
$C_{10}H_{11}O_2HgBr$. Calculated %: Hg 45.21

4 Reaction of (l)-Menthyl Bromo(phenyl)acetate with Mercury

A mixture of 33.4 g (0.09 mole) of (l)-menthyl bromo(phenyl)acetate* and 135 g (0.68 g-atom) of mercury was shaken for 30 minutes. When the reaction mixture had become solid, it was set aside for 2-3 hours, and was then extracted with acetone. The acetone was evaporated off, and the residue was washed with cold alcohol. M.p. (from alcohol) 158-161°, yield 15.5 g (31%). The substance is described for the first time.

Found %: C 39.02; 39.14; H 4.59; 4.55
$C_{18}H_{28}O_2HgBr$. Calculated %: C 39.03; H 4.55

5 Symmetrization of Ethyl (Bromomercuri)phenylacetate

A stream of dry ammonia was passed for 10 minutes into a solution of ethyl (bromomercuri)phenylacetate (8 g) in dry chloroform. The precipitated bromoamidomercury (about 3.5 g) was filtered off, and chloroform was removed from the filtrate under suction. The oil remaining after removal of chloroform crystallized on standing (20-30 hours). The substance was washed with cold petroleum ether and cold methanol. M.p. after two recrystallizations from methanol 105.5-106.5°, yield 2.0 g (42%). The substance is described for the first time.

Found %: Hg 38.39; 38.44
$C_{18}H_{22}O_4Hg$. Calculated %: Hg 38.12

6. Reaction of Ethyl (Bromomercuri)phenylacetate with Acetyl Chloride

Doubly distilled acetyl chloride (31.4 g = 0.4 mole) was added to a suspension of 88.72 g (0.2 mole) of ethyl (bromomercuri)phenylacetate in dry toluene (100 ml). There was no reaction in the cold, and the mixture was heated on a water bath and boiled for two hours, care being taken to exclude moisture. The inorganic precipitate (mercuric halide, 49.2 g) was filtered off, and excess of acetyl chloride, acetic acid, and a great part of the toluene were driven from the filtrate (which was light brown) at atmospheric pressure. The residue was distilled under 18 mm pressure, two fractions being collected:

Fraction I: B.p. 121-125°, 11.8 g.
Fraction II: B.p. 140-160°, 10.4 g

Fraction I boiled mainly at 225-226° under normal pressure and was ethyl phenylacetate. Fraction II was a liquid that rapidly decolorized an alkaline solution of permanganate and a solution of bromine in carbon tetrachloride; its alcoholic solution became violet when ferric chloride was added. With phenylhydrazine in alcoholic solution the phenylhydrazone of ethyl 2-phenylacetoacetate (m.p. 104°) was formed, and the latter, on being heated, yielded 3-methyl-1,4-diphenyl-2-pyrazolin-5-one, melting after being recrystallized twice from alcohol, at 195.5-196° (literature gives 196° [13]).

Found %: N 11.55, 11.34
$C_{16}H_{14}ON_2$. Calculated %: N 11.20

It was thus shown that Fraction II was the C-acetyl(phenyl)acetic ester. In order to find out whether there was any isomeric O-acetyl(phenyl)acetic ester in this fraction, 5 g of it was treated with excess of a 2.5% aqueous solution of KOH in the cold (the mixture was shaken for one hour and then set aside for one day). The oil (1.2 g) that formed on standing, which was found to be ethyl phenylacetate, was separated and hydrolyzed by heating with alkali, yielding phenylacetic acid (0.7 g), m.p. 76° after recrystallization from ligroin. It was concluded on the basis of the yield of phenylacetic ester that Fraction II contained at least 30% of the acetyl derivative of the enol form of phenylacetic ester.

7 Reaction of Ethyl Iodoacetate with Mercury in Presence of Ultraviolet Radiation.

* A freshly prepared (liquid) mixture of diastereoisomers was employed.

A mixture of 5 g of ethyl iodoacetate, 15 ml of dry benzene, and 25 g of mercury was placed in a quartz test tube. The reaction mixture was irradiated for 16 hours with ultraviolet radiation, agitation being provided by a stirrer made from a bottle brush. The inorganic precipitate, consisting of unchanged mercury, mercurous iodide and mercuric iodide, was filtered off and washed with benzene. Benzene was removed from the filtrate under reduced pressure. The oil remaining after removal of benzene crystallized after standing for two weeks in a vacuum desiccator. The crystals were transferred to a porous plate and pressed out. They were recrystallized from methanol. Yield 0.2 g; m.p. 56-57°.

Ethyl iodomercuriacetate is a yellow crystalline substance, readily soluble in hot methanol and hot ethanol, soluble also in acetone and ethyl iodoacetate. Cold concentrated hydrochloric acid decomposes it with formation of mercuric iodide. The substance is described for the first time.

Found %: C 11.50; 11.33; H 1.78; 1.77

$IHgCH_2CO_2C_2H_5$. Calculated %: C 11.57; H 1.72

8. Reaction of Iodobenzene with Mercury

Iodobenzene (10.2 g = 0.05 mole) and mercury (50 g = 0.25 g-atom) were placed in a quartz test tube fitted with a stirrer made from a bottle brush. The mixture was irradiated for 40 hours while being stirred. The precipitate was then filtered off, washed with petroleum ether, and extracted with acetone. Evaporation of the acetone yielded a residue of 1.6 g (8%) of phenylmercury iodide, melting after crystallization from benzene at 266°. (Literature gives 266° [14]). The melting point of a mixture with authentic phenylmercury iodide was not depressed. In addition to phenylmercury iodide, some mercurous iodide was formed.

9. Reaction of 1-Iodonaphthalene with Mercury

A mixture of 12.7 g (0.05 mole) of 1-iodonaphthalene and 50 g (0.25 g-atom) of mercury was shaken for 50 hours in a quartz test tube. The reaction mixture, on being treated as in the previous experiment, yielded 1.4 g (6%) of 1-naphthylmercury iodide, melting after crystallization from a mixture of benzene and alcohol at 184.5° (literature gives 185° [14]). In addition to 1-naphthylmercury iodide, some mercurous iodide was formed.

10. Reaction of Polyhalomethanes with Mercury

a) Reaction of bromoform with mercury in presence of benzoyl peroxide. In a flask fitted with stirrer and dropping funnel, a stirred mixture of 126.5 g (0.5 mole) of bromoform, 20 g (0.1 g-atom) of mercury carried on barium sulfate, and 0.5 g of benzoyl peroxide was heated in a boiling water bath for 8-10 hours, and then, on three occasions separated by intervals of 2-3 hours, a solution of benzoyl peroxide (0.5 g) in bromoform (10 ml) was added. Reaction was complete in 16-20 hours (the precipitate became white). The precipitate was filtered off and extracted with acetone. mercuric bromide (7.0 g) passed into the acetone, and the residue was a mixture of mercurous bromide and barium sulfate. Bromoform was driven from the filtrate (60 mm, 67°), and the residue was found to be impure benzoic acid.

b) Reaction of bromoform with mercury in presence of radiation. A stirred mixture of 126.5 g (0.5 mole) of bromoform and 20 g (0.1 g-atom) of mercury carried on barium sulfate, containing in a quartz flask, was exposed to ultraviolet radiation. Reaction was complete in 28 hours. The reaction mixture was diluted with ether, and the precipitate, consisting of mercuric bromide, mercurous bromide, and barium sulfate, was filtered off. Ether was removed from the filtrate at ordinary pressure, and bromoform was removed at 60 mm. The residue, pentabromoethane, came over at 120°/12 mm; yield 0.5 g; m.p. 52-53° (literature gives 54° [15]).

c) Reaction of bromoform with mercury at 100°. A mixture of bromoform (126.5 g) and mercury (20 g) carried on barium sulfate was heated on a boiling water bath until the precipitate became white (about 60 hours). The reaction mixture was treated as in the previous experiment: mercuric and mercurous bromides were isolated, also 0.3 g of pentabromoethane.

d) Reaction of carbon tetrachloride with mercury in presence of benzoyl peroxide. A mixture of carbon tetrachloride (100 g), mercury (20 g) carried on barium sulfate, and benzoyl peroxide (1 g) was placed in a flask provided with stirrer and a condenser protected by a calcium chloride tube. The reaction mixture was heated at the boil and was stirred continuously, and two 0.5-g portions of benzoyl peroxide were added at intervals of 15 hours. The precipitate became pure white after 50 hours, and it was found to consist of calomel and barium sulfate. The filtrate was evaporated down, and the residue, consisting of hexachloroethane, was distilled (yield 1.5 g). After a second distillation it melted at 185.5-186.5° (literature gives 186.85-187.40° [16]).

e) Reaction of carbon tetrachloride with mercury at 120 - 130°. A mixture of 77 g (0.5 mole) of carbon tetrachloride and 150 g (0.5 g-atom) of mercury carried on barium sulfate was heated in a sealed tube for 40 hours at 120 - 130°. When the tube was opened, a small amount of hydrogen chloride was evolved. The contents of the tube were diluted with ether and the precipitate, which consisted of calomel and barium sulfate, was filtered off. The ether solution was evaporated down and the residue was distilled, yielding pure hexachloroethane (3.5 g, 6 %).

SUMMARY

1. The reactions of several aliphatic and aromatic halogen derivatives with mercury have been investigated.

2. It has been shown that reaction of halogen derivatives with mercury is activated by ultraviolet radiation and by benzoyl peroxide, a fact that is an argument in favor of a homolytic mechanism for these reactions.

3. It has been found that aromatic iodide derivatives, and also aliphatic and aliphatic-aromatic bromine derivatives, can react with mercury with formation of organomercury compounds.

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PRINCIPLES OF THE NOMENCLATURE AND CLASSIFICATION OF MACROMOLECULAR ORGANOSILICON COMPOUNDS

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During the last two decades the chemistry of macromolecular organosilicon compounds has established itself as a feature of the utmost importance in the present and future development of organosilicon chemistry. For its further successful development it is essential to systematize the material that has already accumulated and to work out a scheme of nomenclature and classification of macromolecular organosilicon compounds. The development of a nomenclature and classification for this important section of organosilicon chemistry will facilitate its study and further progress. The names of macromolecular organosilicon compounds are at present formed without any definite system, and they are very often arbitrary and do not reflect the chemical structure of the macromolecular organosilicon compound, it is therefore impossible to get any idea from these names of the properties and possible chemical reactions of the substances. No schemes of nomenclature and classification of macromolecular organosilicon compounds have yet been proposed in the literature.

In one of our papers we have stated the basic principles of our proposed nomenclature and classification of low-molecular-weight organosilicon compounds [1]. It is proposed that our rational nomenclature for macromolecular organosilicon compounds should be based on the structure of the main chain of the macromolecule. The names of macromolecular organosilicon compounds are made up of: numbers and names of end groups, names of groups, radicals, or atoms bound to silicon or other atoms forming links in the chain molecule, with indications of their numbers, names of groups, radicals, or atoms from which the chain of the macromolecule is built up. The number of links in the chain is denoted by the prefix "poly". For end groups an indication is given for their position at the first and terminal atom, namely (1—n). The names of copolymers are built up in a similar way. The silicon atom is called "silane".

Our classification of macromolecular organosilicon compounds is based on the structure of the main chain of the molecule. As a starting point for the classification we take the sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ and all other macromolecular organosilicon compounds are regarded as derivatives of this substance, i.e., as substances formed from it by replacement of hydrogen atoms by organic radicals or groups and, for certain classes of compounds by simultaneous replacement of Si—Si links by bivalent radicals, oxygen, or amino group (—NH—), etc.

When in a polymeric silahydrocarbon hydrogen is replaced by radicals or groups, for example:

	Radicals	Groups
Methyl CH_3-	Chloromethyl $ClCH_2-$	Methoxy CH_3O-
Ethyl C_2H_5-	Chloroethyl $ClCH_2CH_2-$	Ethoxy C_2H_5O-
Propyl C_3H_7-	Chlorophenyl ClC_6H_4-	Phenoxy C_6H_5O-
Butyl C_4H_9-	Vinyl $CH_2=CH-$	Anilino C_6H_5NH- etc.
Phenyl C_6H_5-	Ethynyl $CH\equiv C-$ etc.	

with simultaneous replacement of Si—Si bonds by bivalent radicals (—R—) or bivalent groups (—NH—, —OM—, where M is a metal), or by oxygen atoms, various classes of macromolecular organosilicon compounds are accordingly formed.

The following division into classes is the one that accords most satisfactorily with the present position of the study of macromolecular organosilicon compounds.

1. Silanochain polymers or alkyl(aryl)polysilanes. Silanochain polymers are substances in which the molecular chain is composed entirely of silicon atoms. Substances of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2-]_xSiH_3$ by organic radicals or groups. Their names are built up from the numbers and names of end groups, the names of radicals or groups (the number that occur in the unit of the chain molecule is indicated), the names of atoms from which the main chain of the polymer molecule is built, and the prefix "poly", for example:

$(CH_3)_3S-[Si(CH_3)_2]_x Si(CH_3)_3$

(1—n) Hexamethylpolydimethylsilane

$(CH_3)_3Si[-C_6H_4 Si(CH_3)-]_x Si(CH_3)_3$

(1—n) Hexamethylpolyphenylmethylsilane

$(Si(C_6H_5)CH_2)_x$

Polyphenylmethylsilane

Compounds of this class are obtained by the action of alkali metals on alkyl(aryl)halosilanes, and also by other methods. The silicon chain is destroyed by hydrolysis, especially in an alkaline medium. On pyrolysis, silanochain polymers decompose with formation of low molecular-weight products, readily oxidized by air.

2. Carbosilanochain polymers or organopolyalkyl(aryl)silanes. Carbosilanochain polymers are substances in which the molecular chain is composed of carbon and silicon atoms. Compounds of this class are formed by replacement of hydrogens in the polymeric silahydrocarbon $H_3Si-[SiH_2-]_x SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by bivalent alkyl or aryl radicals. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals or groups of the unit of the chain molecule, and names of radicals and atoms from which the chain of the macromolecule is built, for example:

$(CH_3)_3Si-[CH_2-Si(CH_3)_2-]_x CH_2-Si(CH_3)_3$

(1—n) Hexamethylpolydimethylmethylenesilane

$(CH_3)_3Si[-CH_2-CH_2-Si(C_2H_5)_2-]_x C_2H_4-Si(CH_3)_3$

(1—n) Hexamethylpolydiethylethylenesilane

$(CH_3)_3Si-[C_6H_4-Si(CH_3)_2]_x-C_6H_4-Si(CH_3)_3$

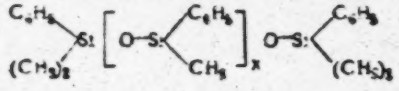
(1—n) Hexamethylpolydimethylphenylenesilane

Compounds of this class are prepared by the action of alkali metals, etc., on alkyl(aryl)halosilanes and dihalo derivatives. The silicon-carbon polymer chain is not broken down hydrolytically by water. On pyrolysis, carbosilanochain polymers very often form low-molecular-weight polymeric compounds having chains of similar structure.

3. Oxygenosilanochain polymers or organopolyalkyl(aryl)siloxanes. Organopolyalkyl(aryl)siloxanes are substances in which the molecular chain is composed of oxygen and silicon atoms. Compounds of this class are formed by replacement of hydrogens in the polymeric silahydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by oxygen. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals and groups attached to silicon in the unit of the chain, and names of radicals and atoms from which the chain of the macromolecule is built:

$(CH_3)_3Si[-OSi(CH_3)_2-]_x-O-Si(CH_3)_3$

(1—n) Hexamethylpolydimethylsiloxane



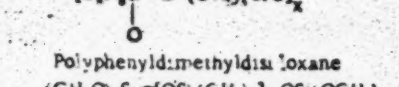
(1—n) Diphenyltetramethylpolyphenylmethylsiloxane

$(CH_3SiO_{1.5})_x$

Polymethylsiloxane

$[(CH_3)_2SiO]_x$

Polydimethylsiloxane



Polyphenyldimethyldisiloxane

$(CH_3O)_2Si-[OSi(CH_3)_2]_x OSi(OCH_3)_3$

(1—n) Hexamethoxypolydimethylsiloxane

$(C_2H_5O)_2Si-[OSi(OC_2H_5)_2-]_x OSi(OC_2H_5)_3$

(1—n) Hexaethoxypolydiethoxysiloxane

$[Si(OC_2H_5)_2O]_x$

Polydiethoxysiloxane

Compounds of this class are obtained by hydrolysis with water of organohalosilanes, organo-substituted esters of silicic acid, and other compounds containing groups attached to silicon that may be split off by hydrolysis; they

may be prepared also by other methods. The oxygenosilane chain of the polymer is not broken down by hydrolysis. Organopolyalkyl(aryl)silcxanes are heat-stable compounds, but at very high temperatures linear polymers depolymerize, often forming low-molecular-weight compounds $(R_2SiO)_x$, where x = 3, 4, 5, 6, etc. On pyrolysis in presence of air, they may be converted into a three-dimensional polymer owing to removal of organic groups and formation of Si—O linkages.

4. Carbonsiloxanochain polymers or organopolyalkyl(aryl)carbosiloxanes. Carbonsiloxanochain polymers are substances in which the molecular chain is composed of carbon, silicon, and oxygen. Compounds of this class are formed by replacement of hydrogens in the sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by organic radicals or groups, with simultaneous replacement of Si—Si links by organic bivalent radicals and oxygen. Their names are built up from the numbers and names of end groups, the prefix "poly", names and numbers of radicals and groups attached to silicon in the unit of the chain, and names of radicals and atoms from which the chain of the macromolecule is built, for example:

$(CH_3)_3Si[-C_6H_4-Si(CH_3)_2OSi(CH_3)_2]_x-C_6H_4-Si(CH_3)_3$

(1—n) Hexamethylpolytetradimethylphenylenedisiloxane

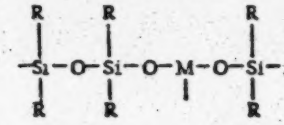
$(CH_3O)_3Si[CH_2-Si(CH_3)_2OSi(CH_3)_2]_x-CH_2-Si(OCH_3)_3$

(1—n) Hexamethoxypolytetramethylmethylenedisiloxane

Compounds of this class are obtained by the action of alkali metals on organohalosilanes and organohalodisiloxanes. they may be prepared also by other methods. The chains of these molecules are not broken down by hydrolysis with water, they are stable to heat, but at high temperatures they undergo pyrolysis with breakdown of the main chain of the molecule.

5. Metallooxygensilanochain polymers or organopolyalkyl(aryl)metallosiloxanes. Metallooxygensilanochain polymers are substances in which the molecular chain is composed of metal atoms, oxygen, and silicon. The metal may be a bi- or multi-valent metal, such as magnesium, aluminum, chromium, lead, tin, etc.

The chain of the molecule can be represented as follows:



Compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by oxygen O or by the —OM— group, where M is a bi- or multi-valent metal. The names of compounds of this class are built up from the names and numbers of end groups, the prefix "poly", the numbers and names of radicals or groups attached to silicon or metal atoms in the unit of the polymer chain, and names of atoms from which the chain of the macromolecule is built, for example:

$(CH_3)_3Si[OAl(O)-OSi(CH_3)_2-]_x\ OAl(O)-O-Si(CH_3)_3$

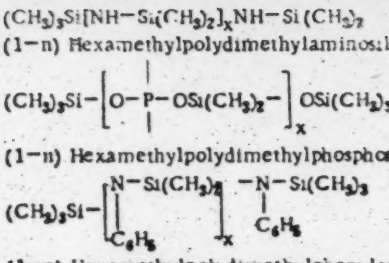
(1—n) Hexamethylpolydimethylaluminosiloxane

$(C_2H_5O)_3Si[OMgOSi(OC_2H_5)_2]_x-OMgOSi(OC_2H_5)_3$

(1—n) Hexaethoxypolydiethoxymagnesiumsiloxane

6. Metalloidoxygensilanochain polymers or organopolyalkyl(aryl)metalloidsiloxanes. Metalloidoxygensilanochain polymers are substances in which the molecular chain is composed of atoms of nitrogen, oxygen, or other metalloid (phosphorus, sulfur, etc.) and silicon atoms. Polymeric compounds of this class are formed by replacement of hydrogens in the polymeric sila hydrocarbon $H_3Si-[SiH_2]_x-SiH_3$ by radicals or groups, with simultaneous replacement of Si—Si links by metalloid atoms, e.g. S, or a metalloid group, e.g. —NH—, —OPO—, etc.

The names of macromolecular organosilicon compounds of this class are built up from the names and numbers of end groups, the prefix "poly", the numbers and names of radicals and groups attached to silicon and metalloid atoms in the unit of the chain polymers, and names of atoms and metalloid groups from which the chain of the macromolecule is built, for example:



(1–n) Hexamethylpolydimethylaminosilane

(1–n) Hexamethylpolydimethylphosphorsiloxane

(1–n) Hexamethylpolydimethylphenylaminosilane

Compounds of this class have received little study: only a few are known. High polymers containing nitrogen are obtained by the action of ammonia or amines on alkylarylhalosilanes. Compounds containing phosphorus in the main chain are obtained by the action of phosphoric anhydride or phosphoric esters on organosilicon compounds containing hydroxyl groups attached to silicon, etc. The chains of these molecules are broken down by hydrolysis with water. On pyrolysis, chain breakdown occurs.

The proposed scheme for the classification of macromolecular organosilicon compounds is not complete, being concerned with principles only: only linear and cyclic polymers have been referred to it, and ramified chains have not been considered, though there can be no doubt that they may be included in this classification.

Also, macromolecular organosilicon compounds containing not only groups or organic radicals, but simultaneously both groups and radicals, may equally readily be incorporated in the proposed scheme of classification. The introduction of any organic group into an organic radical attached to a silicon atom in the unit of the molecular chain does not change the class of the given substance, because the classification is based on the structure of the molecular chain.

All the properties of macromolecular organosilicon compounds are related, to a greater extent than for organic high polymers, to the structure of the main chain of the macromolecule, and classification of the polymers according to the structure of the molecular chain therefore permits their properties to be predicted.

SUMMARY

1. A nomenclature and classification has been proposed for macromolecular organosilicon compounds.

2. The proposed classification of macromolecular organosilicon compounds is based on the structure of the main chain of the molecule.

3. The substance taken as the starting point for the classification is the polymeric sila hydrocarbon $H_3Si[SiH_2]_xSiH_3$, and all other macromolecular organosilicon compounds are treated as derivatives of this substance.

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CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 2. HYDROGENATION OF ISOPRENE IN PRESENCE OF PLATINUM, PALLADIUM, AND NICKEL

B. A. Kazansky, I. V. Gostunskaya, and A. M. Granat

It has been shown by Kazansky and Popova [1] that when biisocrotyl (2,5-dimethyl-2,4-hexadiene) is hydrogenated in presence of platinum, palladium, or Raney nickel, addition of hydrogen occurs simultaneously in all possible ways so that the hydrogenation of biisocrotyl must be classified, according to Lebedev's system, as 1,3-diene hydrogenation of the second type. Addition of hydrogen to biisocrotyl occurs predominantly in the 1,2 positions, although the extent to which it occurs in these positions depends on the nature of the catalyst. In addition to alkenes a certain amount of the full-hydrogenation product, 2,5-dimethylhexane, is always formed at the same time, it is formed to the greatest extent in presence of platinum, which is the least selective of the catalysts in the hydrogenation, and to the least extent in presence of Raney nickel, when hydrogenation proceeds in the most selective fashion, the main reaction product (about 90%) being 2,5-dimethyl-2-hexene. The reaction-rate curves for the hydrogenation of biisocrotyl give little indication of the actual course of the reaction.

The effect of the nature of the catalyst on the manner in which hydrogen added to biisocrotyl, as observed in the work referred to, prompted us to carry out a comparative investigation of the hydrogenation of isoprene in presence of the same catalysts, in spite of the fact that this reaction in presence of platinum black had already been described (1928) by Lebedev and Yakubchik [2], who found that isoprene belongs to Lebedev's second type of dienes.

Lebedev and Yakubchik did not isolate any individual hydrocarbons from the products of the 50% hydrogenation of isoprene, but, having first removed unchanged isoprene with the help of SO_2, they were able to form an idea of the nature of these hydrocarbons by analyzing the kinetic curves obtained for addition of hydrogen to these products to saturation and by determining the amount of hydrogen required (from the difference between the calculated volume of hydrogen and that actually found it was possible to estimate the content of isopentane in the products of the first stage of hydrogenation). By addition of 50% (one molecule) of hydrogen, isoprene may yield a mixture of 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene, and these may be further hydrogenated at different rates [3] giving rise to separate sections on the kinetic curves for the reaction. It was therefore possible, by adding definite amounts of 3-methyl-1-butene or 2-methyl-2-butene to the hydrogenation product freed from isoprene and then hydrogenating the mixture, to determine (by a comparison of the results found in this way with those obtained from the analysis of kinetic curves obtained without these additions) the contents of these hydrocarbons in the products under investigation.

On the basis of all the results obtained by this means, Lebedev and Yakubchik concluded that the composition of the product formed by the addition of one molecule of hydrogen to isoprene in presence of platinum black was:

Isoprene	30 mol.-%
Isopentane	30 "
3-Methyl-1-butene	12 "
2-Methyl-1-butene	13 "
2-Methyl-2-butene	15 "
	100 "

Apart from this work of Lebedev, there has been a study of the catalytic hydrogenation of isoprene by Dupont [4], who used Raney nickel as catalyst. The mixture of hydrogenation products that he obtained was investigated by

the Raman spectra method, and it was found to contain equimolecular amounts of 3-methyl-1-butene and 2-methyl-1-butene. The absence in Dupont's hydrogenation products of 2-methyl 1-butene is puzzling and gives rise to some doubts concerning the accuracy of the analysis.

In the present investigation our object was the determination of the composition of the products of the addition of one molecule of hydrogen to isoprene in presence of platinum, palladium and Raney nickel by separating the components of the mixture by distillation through a column having an efficiency of about 70 theoretical plates. The main difficulty that we have met has arisen from the volatility of the hydrocarbons (b.p. 20-39°), which resulted in losses during the treatment of the mixture (mainly during washing, separation, transference operations, etc.), in spite of the cooling employed. Since the losses during distillation through the columns were comparatively low, we consider that they may be assigned in more or less equal measure to all of the components of the mixture.

As a result of rate measurements on the hydrogenation of isoprene in presence of the three catalysts, hydrogenation curves were obtained which differed from one another in character. The curves for hydrogenation in presence of platinum black had breaks corresponding to the addition of 70% hydrogen and the consumption of the whole of the isoprene. Lebedev called this point "the critical point for the hydrogenation of a conjugated system". The curves for hydrogenation of isoprene in presence of palladium black and Raney nickel showed one break, which in the case of palladium occurred somewhat beyond the point corresponding to the addition of one molecule of hydrogen (50%) and in the case of Raney nickel corresponded exactly to the addition of one molecule of hydrogen. It might have been supposed from the curves, following Lebedev's classification, that hydrogenation in presence of these two last catalysts proceeds in a fairly selective fashion, but a detailed investigation of the reaction products has shown that here as in the case of platinum the addition of hydrogen goes in all possible ways. The part played by the nature of the catalyst is to be seen first in the fact that during the addition of the first molecule of hydrogen the fully-saturated hydrocarbon is formed in smaller amount when palladium black or Raney nickel is used than when platinum black is used (2-3% instead of 25-30%), and second, in the fact that with different catalysts the three pentenes are formed in different proportions. Thus, in the case of platinum black the main reactions were 3,4-addition of hydrogen to form 2-methyl-1-butene and addition of two molecules of hydrogen to give isopentane; in the case of palladium black the main reaction was 1,4-addition of hydrogen with formation of 2-methyl-2-butene; and in the case of Raney nickel the main reaction was again 1,4-addition of hydrogen, but some 3,4-addition with formation of 2-methyl-1-butene, occurred also.

In comparison with bisocrotyl, isoprene, which may be regarded as butadiene with one substituent on the second carbon atom, takes up more hydrogen at the first and fourth carbon atoms during hydrogenation, the difference is particularly notable when palladium and nickel catalysts are used. Similar peculiarities with respect to the direction of reaction, though in a more clearly expressed form, are observed for the addition of nascent hydrogen to these two hydrocarbons: under the action of hexammine calcium bisocrotyl again unites with hydrogen mainly in the 1,2 positions [5] (the same is to be observed for reaction with the system sodium-liquid ammonia [6]); under these conditions isoprene unites with hydrogen mainly in the 1,4 positions [5].

EXPERIMENTAL

1 Characteristics of the isoprene used. The isoprene was distilled through a laboratory rectification column of 70-plate efficiency, and it had the following properties: b.p. 33.5° at 750 mm; n_D^{20} 1.4224; d_4^{20} 0.6798, found MR 24.45, calculated for C_5H_8 24.33; molecular refraction increment 1.12. The literature [2] gives: b.p. 34.5° at 765 mm; n_D^{20} 1.42207; d_4^{20} 0.6803, found MR 24.40, calculated for C_5H_8 24.33.

2 Procedure for hydrogenation and investigation of reaction products. The isoprene was hydrogenated at room temperature and atmospheric pressure in a long-necked flask shaken about 300 times (double shakes) per minute. The amount of hydrogen absorbed was measured in a 100-ml gas burette having 0.2-ml graduations. The readings required for constructing the hydrogenation curve were taken every 30 seconds. Completion of the addition of the first molecule of hydrogen is indicated on the hydrogenation curves by the symbol X.

Platinum and palladium blacks were prepared by Willstätter's method [7], and Raney nickel was prepared by Adkins' method [8]. The solvent was 96% alcohol. In experiments having as their object the study of the products resulting from the addition of one molecule of hydrogen to isoprene, the reaction was allowed to proceed until the calculated amount of hydrogen for the given weight of isoprene had been absorbed, and the catalyst was then filtered off and the alcoholic solution of the hydrogenation products was distilled through a column to separate the azeotropic mixtures of alcohol with hydrocarbons formed during the hydrogenation. The alcohol was washed out with cooled calcium chloride solution. Isoprene was then removed from the mixtures of hydrocarbons formed in presence of platinum and palladium by treatment in accordance with the Diels-Alder reaction with maleic anhydride

in a benzene medium, since the presence of isoprene would render the further separation of the mixture difficult, and the hydrocarbons were finally fractionated through a column of 70 theoretical plates. The hydrocarbons obtained were identified with the aid of determinations of the boiling points, refractive indices, densities, and bromine numbers of the fractions. Bromine numbers were determined by Kaufmann's method, as modified by Galpern and Vinogradova [10]. The amounts of various hydrocarbons obtained in the hydrogenation process were calculated by using the data supplied by the distillation curves and by making use of the properties of functions.

3. Hydrogenation of isoprene in presence of platinum black. The conditions under which the hydrogenation of isoprene was carried out in two experiments are given in Table 1.

TABLE 1

Expt. No.	Amt. of isoprene (mole)	Amt. of Pt (mole)	Amt. of alcohol (ml)	Temp. of expt (°C)	Pressure (mm Hg)	Amt. of hydrogen (ml)	
						Absorbed	Calculated
1	0.0127	0.0011	25	19	748	670	618
2	0.0105	0.0012	25	22	754	536	512

The hydrogenation curve (Fig. 1) shows that the course of the process is complex. The addition of one molecule of hydrogen is not indicated in any way by the course of the curve; change in rate of hydrogenation begins after the addition of about 70% of hydrogen. As in the hydrogenation curve obtained by Lebedev, four sections can be distinguished in the curves obtained in the present work.

TABLE 2

Fraction No.	B.p. (°C/760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR		Bromine No.*	Amount	
					Found	Calc'd		of alkenes (%)	of isopentane (g)
I	19.9-27.7	3.2	1.3635**	0.6301**	—	—	99.0	43.2	1.8
II	27.8	2.5	1.3553**	0.6176**	25.44	25.29	18.5	8.1	2.3
III	27.9-31.1	3.6	1.3618	0.6284	—	(C_5H_{10})	67.1	29.4	2.5
IV	31.2	4.3	1.3780	0.6500	24.65	24.82 (C_5H_{10})	—	—	—
V	31.3-38.4	2.1	1.3844	0.6583	—	—	—	—	—
VI	38.4-39.9	2.4	1.3887	0.6606	—	—	—	—	—
Residue	—	5.0	1.5000	—	—	—	—	—	—

* In the bromine number column results are given only for the fractions containing saturated hydrocarbons; the bromine numbers of the remaining fractions are close to the theoretical values.

** At 15°.

In order to make a more detailed study of the hydrogenation of isoprene in presence of platinum black, a 50% hydrogenation was carried out on 44.8 g of isoprene. After distillation, removal of alcohol by washing, and removal of isoprene by means of maleic anhydride, the mixture of hydrogenation products with an addition of benzene from the previous treatment was distilled through a column of 70 theoretical plates. Six fractions were obtained; their characteristics are given in Table 2, and the distillation curve is given in Fig. 2.

The physical properties of the hydrocarbons that may be formed by addition of hydrogen to isoprene are given in Table 3 [11].

By taking into account the properties of the fractions obtained and the properties of the hydrocarbons cited in Table 3, we may calculate the compositions of the mixtures of hydrogenation products.

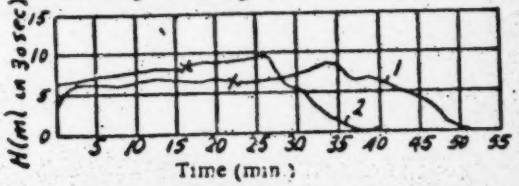

Fig. 1. Hydrogenation curves for isoprene in presence of platinum black. 1) Expt. 1; 2) expt. 2.

Fraction I contains 1.4 g 3-methyl-1-butene and 1.8 g isopentane
Fraction II contains 0.2 g 3-methyl-1-butene and 2.3 g isopentane
Fraction III contains 1.1 g 2-methyl-1-butene and 2.5 g isopentane
Fraction IV contains 4.3 g 2-methyl-1-butene
Fraction V contains 0.8 g 2-methyl-1-butene and 1.3 g 2-methyl-2-butene
Fraction VI contains 2.4 g 2-methyl-2-butene
The residue in the flask is benzene.

Adding together the contents of each individual hydrocarbon in the various fractions and taking into account

TABLE

Hydrocarbon	B.p. (°C at 760 mm)	d_4^{20}	n_D^{20}
3-methyl-1-butene	20.1	0.6340 (15°)	1.3677 (15°)
2-methyl-1-butene	31.0	0.6504	1.3785
2-methyl-2-butene	38.6	0.6596	1.3876
Isopentane	27.9	0.6196	1.3579 (15°)

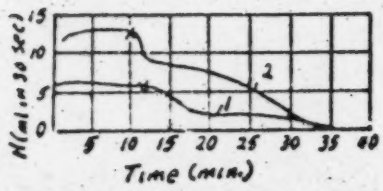

Fig. 3. Hydrogenation curves for isoprene in presence of palladium black. 1) Expt. 1. 2) Expt. 2.

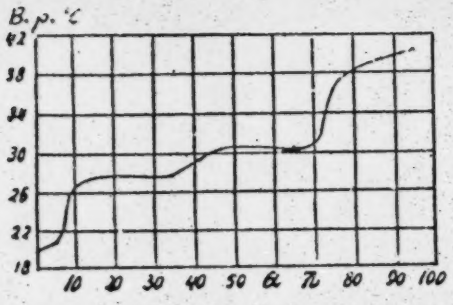

Fig. 2. Distillation curve for the product of the addition of one molecule of hydrogen to isoprene in presence of platinum

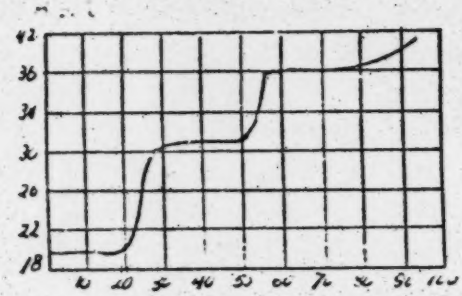

Fig. 4. Distillation curve for the product of the addition of one molecule of hydrogen in presence of palladium

Lebedev's rule, namely that the molar quantities of diene and saturated hydrocarbons at the point at which one molecule of hydrogen has added to the diene are equal, we obtain the following composition for the mixture of hydrogenation products:

3-Methyl-1-butene	1.6 g	7.0 mol %
2-Methyl-1-butene	6.2 g	26.0 "
2-Methyl-2-butene	3.7 g	15.0 "
Isoprene	6.2 g	26.0 "
Isopentane	6.6 g	26.0 "

It will be seen from this that 50% hydrogenation of isoprene in presence of platinum black proceeds in all theoretically possible directions, but the major products are isopentane and 2-methyl-1-butene, the product of the addition of one molecule of hydrogen in the 3,4 position of the conjugated system.

TABLE 4

Expt No	Amt of isoprene (mole)	Amt of Pd (mole)	Amt of alcohol (ml)	Temp (°C)	Pressure (mm Hg)	Amt of hydrogen (ml) Absorbed	Calculated
1	0.0060	0.0008	25	21.0	754	272	292
2	0.0103	0.0020	25	23.5	752	512	506

4. Hydrogenation of isoprene in presence of palladium black. The conditions under which the two experiments were carried out are given in Table 4.

The hydrogenation curves for isoprene in presence of palladium black (Fig. 3) show a break slightly beyond the point for the addition of one molecule of hydrogen. After the break the rate of hydrogenation falls sharply and then gradually. In order to make a more detailed study of the products of the addition of one molecule of hydrogen to isprene in presence of palladium 44.3 g of isoprene was hydrogenated. The hydrogenation product was separated from alcoholic solution and freed from isoprene in the manner already described. Fractionation through a column of 70 theoretical plates gave the curve shown in Fig. 4. The results of the fractionation and the properties of the fractions obtained are given in Table 5.

On the basis of the properties of the fractions obtained, their bromine numbers and the properties of the individual hydrocarbons that can be formed by hydrogenation of isoprene, a calculation was made of the composition of the mixture of hydrogenation products in the same way as that done for the platinum experiment. The

results obtained were:

3-Methyl-1-butene	25 mol. %
2-Methyl-1-butene	30 "
2-Methyl-2-butene	41 "
Isopentane	2 "
Isoprene	2 "

TABLE 5

Fraction No.	B.p (°C/760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR found	MR calculated for C_5H_{10}	Bromine No.	Amount of alkenes (%)	Amount of isopentane (g)
I	20.1-20.2	2.9	1.3685 (15°)	0.6320 (15°)	24.92	24.82	–	–	–
II	20.3-28.6	1.3	1.3675 (15°)	0.6379 (15°)	–	–	198.3	84.1	0.2
III	28.7-30.9	1.0	1.3739	0.6489	–	–	–	–	0.2*
IV	31.0-31.1	2.9	1.3785	0.6506	24.82	–	–	–	–
V	31.2-38.3	2.3	1.3834	0.6566	–	–	–	–	–
VI	38.4-38.5	3.5	1.3879	0.6615	24.92	–	–	–	–
VII	38.6-40.0	1.8	1.3887	0.6618	–	–	–	–	–
	Residue	3.4	1.5022		–	–	–	–	–

TABLE 6

Expt. No.	Amt. of isoprene (mole)	Amt. of Ni(mole)	Amt. of alcohol (ml)	Temp. of expt. (°C)	Pressure (mm Hg)	Amt. of hydrogen (ml) absorbed	Amt. of hydrogen (ml) calculated
1	0.0066	0.0028	30	20.5	759	218**	318
2	0.0067	0.0015	30	20.8	748	190**	328

Hydrogenation of isoprene in presence of palladium black proceeds therefore in all possible directions, but the main direction of the reaction is the addition of one molecule of hydrogen in the 1,4 position of the conjugated system with formation of 2-methyl-2-butene.

5. Hydrogenation of isoprene in presence of Raney nickel. The conditions under which the two experiments were carried out are given in Table 6.

The hydrogenation curves for isoprene in presence of a nickel catalyst are similar in character to those obtained in the presence of palladium black, but the break occurs exactly at the point corresponding to addition of one molecule of hydrogen to isoprene (Fig. 5).

TABLE 7

Fraction No.	B.p. (°C/760 mm)	Amt. (g)	n_D^{20}	d_4^{20}	MR found	MR calculated for C_5H_{10}	Bromine No.	Amount of alkenes (%)	Amount of isopentane (g)
I	20.0-20.1	4.4	1.3672 (15°)	0.6316 (15°)	25.05	24.82	–	–	–
II	20.2-27.3	0.9	1.3636 (15°)	0.6305 (15°)	–	–	218.5	95.5	0.04
III	27.4-31.0	3.4	1.3712	0.6397	–	–	183.5	80.2	0.68
IV	31.1	9.1	1.3783	0.6502	24.84	–	–	–	–
V	31.2-38.3	4.0	1.3936***	0.6595	–	–	–	–	–
VI	38.4	10.8	1.3882	0.6606	25.00	–	–	–	–
VII	38.4-46.2	1.3	1.3883	0.6605	–	–	–	–	–

* The content of saturated hydrocarbon in Fraction III was calculated from the density and refractive index, since it was not found possible to determine the bromine number of the fraction.

** In view of the fact that hydrogenation proceeded at a very low, but constant rate in its final stage, the reaction was not completed.

*** The high refractive index of Fraction V is to be explained by the presence of some isoprene as impurity

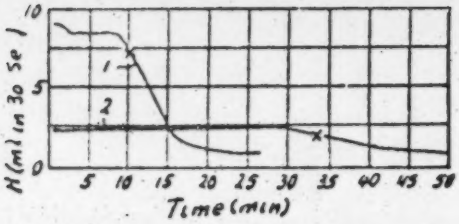

Fig. 5. Hydrogenation curves for isoprene in presence of Raney nickel. 1) Expt. 1. 2) Expt. 2.

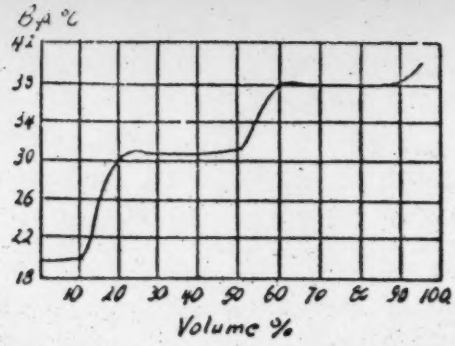

Fig. 6. Distillation curve for the product of the addition of one molecule of hydrogen to isoprene in presence of nickel.

In order to make a detailed study of the hydrogenation of isprene in presence of Raney nickel, 45.1 g of isoprene was hydrogenated. The products of the addition of one molecule of hydrogen to isoprene were treated as before, with the exception of the operation of removing isoprene with the aid of maleic anhydride, as it was considered to be absent from the mixture. It was found that there was actually a small amount of isoprene in the reaction products.

Fraction of the products of the hydrogenation of isoprene in presence of nickel (after separation from alcoholic solution) gave the results shown in Table 7 (curve in Fig. 6). In order to effect a more complete distillation of the hydrocarbons obtained, 6 ml of cyclohexane was added to the mixture to be fractionated.

Calculation of the contents of individual hydrocarbons formed by the addition of one molecule of hydrogen to isoprene in presence of nickel gave the following results:

3-Methyl-1-butene	16 mol. %
2-Methyl-1-butene	40 "
2-Methyl-2-butene	40 "
Isopentane	2 "
Isoprene	2 "

Addition of hydrogen to isoprene in presence of Raney nickel proceeds, therefore, in all possible directions. Addition proceeds mainly in the 1,4- and 3,4-positions of the conjugated system with formation of 2-methyl-2-butene and 2-methyl-1-butene respectively.

SUMMARY

1. Hydrogenation of isoprene in presence of palladium and nickel proceeds, as in the case of hydrogenation in presence of platinum studied previously by Lebedev, as a diene hydrogenation of the second type.

2. For addition of hydrogen in presence of platinum, lower selectivity is observed than in presence of palladium and nickel, which are very similar to one another in this respect.

3. The forms of the hydrogenation rate curves are in no case characteristic of the actual course of the reaction.

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* See Consultants Bureau Translation, p. 409.

REACTIONS OF INDIVIDUAL HYDROCARBONS IN CONTACT WITH ACTIVATED TROSHKOV CLAY

COMMUNICATION 1. REACTIONS OF CYCLOHEXENE, 4-METHYLCYCLOHEXENE, AND 1-OCTENE

N. I. Shuikin and E. A. Timofeeva

The reactions of unsaturated hydrocarbons in contact with synthetic aluminosilicates have been studied in some detail [1-7]. They consist in redistribution of hydrogen (leading to formation of aromatic and saturated hydrocarbons), accompanied by reactions of dehydrocyclization, isomerization, condensation to give higher-boiling products and coke, and scission of carbon–carbon bonds; simultaneously carbonaceous deposits are formed on the catalyst. Thus, catalyzates obtained from cyclohexene in presence of aluminosilicate catalysts have been shown to contain methylcyclopentenes, methylcyclopentane, and a number of aromatic hydrocarbons, the concentration of which increased when the reaction temperature was raised; at the same time, a considerable proportion of the cyclohexene was converted into higher-boiling products and coke.

From cyclohexene at 400° in presence of an SiO_2–Al_2O_3–ThO_2 catalyst, Bloch and Thomas [2] obtained 97.1% of liquid catalyzate, which contained:

C_5 and C_6 alkanes	3.5%
Methylcyclopentane	26.3%
Methylcyclopentenes	23.5%
Cyclohexene	1.5%
Higher-boiling hydrocarbons (including 7% of dimethylnaphthalene)	42.2%

Greensfelder and Voge [3] studied the reactions of cyclohexene in presence of a catalyst of aluminum and zirconium silicates at 500°. They concluded that the main reactions were isomerization, saturation by hydrogen, formation of higher-boiling products and coke, and cracking.

In studies of the behavior of butenes, pentenes, hexenes, and octenes in presence of various samples of aluminosilicate catalyst it has been found that they undergo far-reaching changes: isomerization with subsequent hydrogenation of the products, partial condensation to form larger molecules, scission at carbon–carbon links, and in some cases, conversion into aromatic hydrocarbons.

Maslyansky and Veltistova [4] heated a mixture of n-butenes at 370° in presence of a synthetic aluminosilicate catalyst and obtained, as the main product, a mixture of octenes, which was accompanied by 19% of aromatic hydrocarbons, the content of which in the catalyzate increased to almost double this value (to 37.2%) when the temperature was raised to 450°. Among the gaseous products an appreciable amount of isobutane was found.

Thomas [1] studied the reactions of octenes in presence of a catalyst of aluminum and zirconium silicates at 375°. Apart from alkenes, the catalyzate was found to contain 7-13% of aromatic hydrocarbons, 55-63% of alkanes, and 4-13% of cycloalkanes. The author pointed out that the cracking that occurs tends to lead to the preferential formation of C_3 and C_4 hydrocarbons, rather than C_1 and C_2.

Petrov and Frost [7] found that at 250° in presence of an aluminosilicate catalyst 1-octene was converted almost entirely into a mixture of octenes and octanes of branched structure, among the principal members of which were 2-methyl- and 3-methyl-heptanes.

Practically no study has been made of the behavior of individual hydrocarbons in presence of natural aluminosilicates, in spite of the fact that the latter are just as important for the treatment and purification of petroleum products as the synthetic aluminosilicates. In a previous investigation [8] we have shown that a natural aluminosilicate, activated Troshkov clay, is a good catalyst for the refinement of the middle fraction (170-300°) of the primary tar from Budagov sapropelites. At 450° and at a space velocity of 0.3, a considerable part of the unsaturated hydrocarbons of this fraction are converted into aromatics. Troshkov clay possesses also good desulfurizing properties [9].

In this investigation we decided to study the behavior of individual hydrocarbons in presence of activated Troshkov clay, and as a result we have determined the nature of the reactions given by cyclohexene, 4-methylcyclohexene, and 1-octene. In presence of activated Troshkov clay these hydrocarbons undergo the reactions of isomerization, hydrogenation, dehydrocyclization, condensation to products of higher molecular weight, and partial breakdown at carbon–carbon links.

EXPERIMENTAL

Original hydrocarbons. Cyclohexene and 4-methylcyclohexene were prepared by the dehydration of cyclohexanol and 4-methylcyclohexanol respectively in presence of concentrated sulfuric acid. 1-Octene was prepared by the dehydration of 1-octanol in presence of aluminum oxide at 350°. After being carefully dehydrated and distilled over sodium through a column having an efficiency of 70 theoretical plates, the hydrocarbons had the properties given in Table 1.

TABLE 1

Properties of Hydrocarbons

Hydrocarbon	B.p. (°C; corr.)	n_D^{20}	d_4^{20}	Iodine No.
Cyclohexene	82.5–83.5	1.4470	0.8111	311
Methylcyclohexene	102.0–104.0	1.4435	0.8040	264
Octene	122.5–124.0	1.4120	0.7170	220

The values of the constants indicate that the second hydrocarbon consisted essentially of 4-methylcyclohexene, and the third of 1-octene.

Experimental conditions and analytical procedure. The catalysis reaction was carried out in the usual flow-type apparatus at 450°, at atmospheric pressure, and with a space velocity of 0.3. The catalyst was prepared from activated Troshkov clay, activation being effected by means of sulfuric acid (the composition of the clay is given in our previous paper [8]). All the experiments were carried out with the same sample of catalyst, and the catalyst was regenerated after each experiment by passing air through it at 500° for 5–6 hours. The receiver for the catalyzate was cooled with a mixture of ice and salt, and the trap provided after the receiver was cooled with solid carbon dioxide in acetone. The gas formed was analyzed.

Refractive index, specific gravity, content of sulfonatables, and Margosches iodine number were determined for the liquid catalyzates. The adsorption method was used for the separation of the alkane–cycloalkane part of the catalyzate from the aromatic and unsaturated hydrocarbons. We found that, when the mixture under investigation contained a small amount of unsaturated hydrocarbons, these, on being adsorbed in silica gel, were to be found almost entirely in the aromatic part of the mixture. It was thus possible to separate the catalyzate into an alkane–cycloalkane part and a mixture of aromatic and unsaturated hydrocarbons.

The fractionation curves for the catalyzates and for their alkane–cycloalkane parts were obtained with the aid of a column of 70-plate efficiency, and the curves for the mixtures of aromatic and unsaturated hydrocarbons with the aid of a 20-plate column. The broken lines on the fractionation graphs indicate that in this temperature range the liquid was distilled not through the column, but from small flasks provided with Vigreux columns.

Catalytic reactions of cyclohexene. The cyclohexene was passed in portions of 50 ml (40.6 g) at a time. Two experiments were carried out, the catalyzates being united. Their properties are given in Table 2.

TABLE 2

Properties of Cyclohexene Catalyzates

Expt. No.	Amt. of catalyzate (g)	Yield of catalyzate (% by wt.)	Yield of gas (liters at STP)	n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
1	34.7	85.6	2.53	1.4700	0.8460	45.0	1.1
2	35.4	87.1	2.00	1.4690		45.0	1.2

Analysis of the Gas

Unsaturated hydrocarbons	15.9%
Hydrogen	29.9%
Paraffin hydrocarbons	54.2%

The catalyzate (55 ml, i.e. 45.5 g) was separated by adsorption on silica gel into aromatic and alkane–cycloalkane parts. The iodine number of the aromatic part was 2.5; it sulfonated completely. A formolite test on the alkane–cycloalkane part was negative. The fractionation curves for the two parts of the catalyzate are given in Fig. 1 and 2.

The alkane-cycloalkane part of the catalyzate was fractionated. The results of the fractionation and the properties of the fractions are given in Table 3.

Raman spectrum analysis, which was carried out by M. L. Batuev, showed that the first two fractions consisted

essentially of methylcyclopentane, which was satisfactorily confirmed also by the properties of these fractions. On the basis of the comparatively low aniline point of Fraction III, we may suppose that this also consisted of cycloalkanes. The aromatic part of the catalyzate was separated into two fractions, the properties of which are given in Table 4.

TABLE 3

Properties of Fractions of the Alkane–Cycloalkane Part of the Cyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (% by weight)	Properties n_D^{20}	Properties d_4^{20}	Properties aniline point
I	58.8 – 71.2	5.2	26.0	1.4095	0.7431	35.6
II	71.2 – 71.5	11.6	51.2	1.4088	0.7496	35.2
III	71.5 – 156.0	5.0	22.2	1.4312	0.7813	58.0
Residue	–	0.2	0.6	–	–	–

TABLE 4

Properties of Fractions of the Aromatic Part of the Cyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (% by weight)	n_D^{20}
I	110–160	3.9	19.2	1.4990
II	160–276	16.2	79.5	1.5570
Residue	–	0.3	1.3	–

Treatment of cyclohexene in contact with activated Troshkov clay as catalyst at 450° results therefore in a catalyzate containing 47% of aromatic hydrocarbons, the bulk of which boils above 160°. Benzene is not formed at all, toluene may be formed in traces and very little of the xylenes or ethylbenzene is obtained. (See Fig. 2). In addition, 41% of methylcyclopentane was found in the catalyzate. The remaining 12% of the catalyzate was not identified, but this evidently consisted also of cycloalkanes. In the catalysis process about 14% of the original cyclohexene decomposed with formation of gaseous hydrocarbons and coke. The gas collected for analysis, consisted of 29.9% of hydrogen, 15.9% of unsaturated hydrocarbons, and 54.2% of paraffin hydrocarbons.

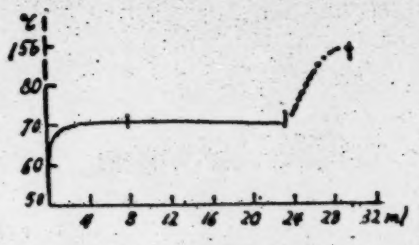


Fig. 1. Fractionation curve for the alkane–cycloalkane part of the cyclohexene catalyzate.

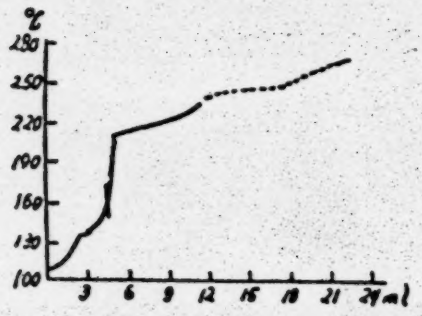


Fig. 2. Fractionation curve for the aromatic part of the cyclohexene catalyzate.

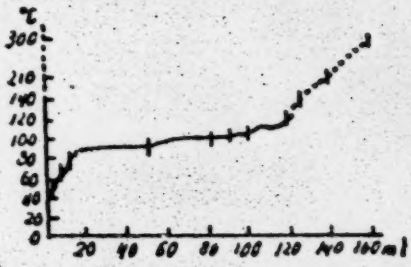
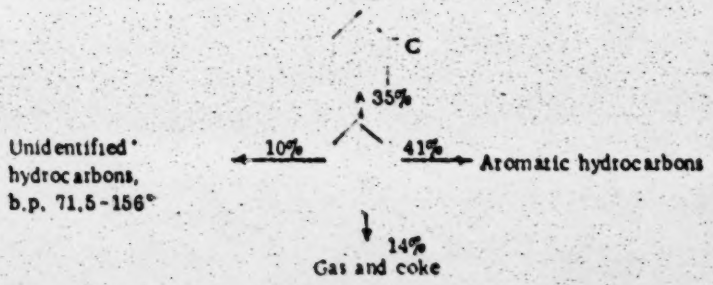


Fig. 3. Fractionation curve for the methylcyclohexene catalyzate.

The catalytic reactions of cyclohexene under the conditions of our experiments may be represented diagrammatically as follows (the percentages refer to the original hydrocarbon):



Catalytic reactions of 4-methylcyclohexene. In the first two experiments methylcyclohexene was passed in portions of 100 ml (80.4 g); in the third experiment, 120 ml (96.5 g) of this hydrocarbon was taken. The results obtained are given in Table 5.

TABLE 5

Properties of Catalyzates from 4-Methylcyclohexene

Expt. No.	Amt. of catalyzate (g)	Yield of catalyzate (% by wt.)	Yield of gas (liters STP)	n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
1	71.2	88.5	1.42	1.4550	0.8050	55.0	72.4
2	69.9	87.0	1.35	1.4530	0.8012	53.0	71.2
3	83.8	86.8	1.38	1.4535	0.8020	56.0	73.0

Analysis of the Gas

Unsaturated hydrocarbons	28.4%
Hydrogen	18.3%
Paraffin hydrocarbons	53.3%

Part of the united catalyzate (170 ml, i.e., 136.5 g) was fractionated through a 70-plate column into narrow fractions (Fig. 3). The properties of these fractions are given in Table 6.

TABLE 6

Properties of Fractions of the 4-Methylcyclohexene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (% by weight)	n_D^{20}	d_4^{20}	Iodine No.	Content of unsat. hc. (% by wt.)	Content of sulfonatable hc. (% by wt.)	Content of aromatic hc. (% by wt.)
I	27.9-50.9	2.6	1.9	—	—	—	—	—	—
II	50.9-66.4	3.5	2.6	1.3920	0.6959	80.6	27	26	absent
III	66.4-79.1	2.8	2.1	1.4170	0.7564	62.1	31	39	8
IV	79.1-91.9	28.4	21.1	1.4109	0.7464	25.8	10	12	2
V	91.9-100.9	23.8	17.7	1.4230	0.7683	46.7	18	18	absent
VI	100.9-102.9	8.5	6.3	1.4252	0.7756	30.3	13	13	absent
VII	102.9-104.9	6.6	4.9	1.4360	0.7914	79.2	35	34	absent
VIII	104.9-122.0	17.1	12.7	1.4750	0.8405	54.1	24	89	65
IX	122.0-149.0	5.0	3.7	1.4680	0.8303	40.5	20	79	59
X	149.0-210.0	12.3	9.1	1.5025	0.8785	7.4	4	100	96
XI	210.0-302.0	19.3	14.3	1.5720	0.9646	—	absent	100	100
XII	residue	4.8	3.6	Thick resinous dark-colored liquid					

The properties of the fractions after removal of aromatic and unsaturated hydrocarbons by sulfonation are given in Table 7.

The results given in Tables 6 and 7 enable us to characterize the fraction as follows:

Fraction I boiling range 27.9-50.9°. Very volatile mobile liquid containing unsaturated hydrocarbons. Not investigated owing to lack of material.

Fraction II, boiling range 50.9-66.4°; consisted of 26-27% of unsaturated and 74-73% of saturated hydrocarbons. It may be supposed that hexenes and possibly methylcyclopentenes entered into the composition of the unsaturated part. The properties of the saturated part of the fraction indicate that it contained isomers of hexane.

Fraction III, boiling range 66.4-79.1°; contained 31% of unsaturated hydrocarbons, 8% of benzene, and 61% of saturated hydrocarbons. The main part of the saturated hydrocarbons evidently consisted of methylcyclopentane.

Fraction IV, boiling range 79.1-91.9°; consisted of 10% of unsaturated hydrocarbons, 2% of benzene, and 88% of saturated hydrocarbons. After removal of aromatic and unsaturated hydrocarbons, the fraction boiled within the range 89.3-90.5° (through a column of 70 theoretical plates, with decane as carrier), and it could therefore be concluded that 1,3-dimethylcyclopentane was to be found in the saturated part. The aniline point and refractive index confirmed this conclusion.

Fraction V, boiling range 91.9-100.9°; contained 19% of unsaturated and 82% of saturated hydrocarbons. After removal of unsaturated hydrocarbons the fraction boiled over the range 92.0-99.0°. The boiling range, aniline point, specific gravity, and refractive index corresponded to 1,2-dimethylcyclopentane.

Fraction VI, boiling range 100.9-102.9°; consisted of 13.0% of unsaturated and 87.0% of saturated hydrocarbons (evidently a mixture of 1,2-dimethylcyclopentane and ethylcyclopentane).

Fraction VII, boiling range 102.9-104.9°; contained 35% of unsaturated and 65% of saturated hydrocarbons (judging from the properties—ethylcyclopentane).

Fraction VIII, boiling range 104.9-122.0°; consisted of 65% of toluene, 24% of unsaturated hydrocarbons, and 11% of cycloalkanes.

Fraction IX, boiling range 122.0-149.0°; contained 59% of aromatic, 20% of unsaturated, and 21% of saturated hydrocarbons.

Fraction X, boiling range 149.0-210°, and Fraction XI, boiling range 210-302°; consisted almost entirely of aromatic hydrocarbons.

TABLE 7

Properties of Fractions of the 4-Methylcyclohexene Catalyzate after the Removal of Aromatic and Unsaturated Hydrocarbons.

Fraction Number	n_D^{20}	d_4^{20}	Aniline point
II	1.3722	0.6550	74.1
III	1.4111	—	36.0
IV	1.4102	0.7480	46.2
V	1.4253	0.7718	40.9
VI	1.4227	0.7682	39.3
VII	1.4200	0.7650	38.0
VIII	1.4190	0.7708	48.7
X	1.4285	—	—

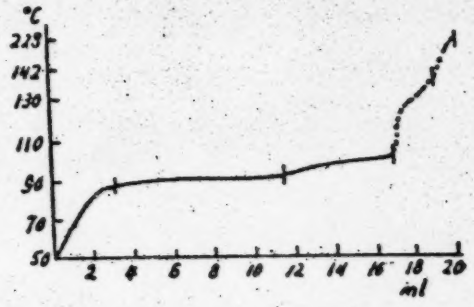


Fig. 4. Fractionation curve for the alkane—cycloalkane part of the methylcyclohexene catalyzate.

Another part of the 4-methylcyclohexene catalyzate (60 ml, i.e., 48.2 g) was passed through silica gel, isopentane being used as displacing liquid. The alkane-cycloalkane part of the catalyzate gave a negative formolite test and had an iodine number of 1.2. The whole of the mixture of aromatic and unsaturated hydrocarbons underwent sulfonation, and the iodine number of the mixture was 35.8. It may therefore be considered that the separation of the catalyzate went satisfactorily. The fractionation curves of the two parts of the catalyzate are shown in Fig. 4 and 5.

The properties of the fractions obtained from the alkane—cycloalkane part of the catalyzate are given in Table 8. The properties of the fractions isolated from the mixture of aromatic and unsaturated hydrocarbons in the catalyzate are given in Table 9.

The results given in Tables 8 and 9 confirm our conclusions concerning the composition of the saturated and aromatic hydrocarbons in the narrow fractions of the catalyzate. Fraction II (Table 8), judging by its properties, consisted almost entirely of 1,3-dimethylcyclopentane, and Fraction III — mainly of 1,2-dimethylcyclopentane.

Hence, 4-methylcyclohexene in contact with activated Troshkov clay undergoes far-reaching changes, as a result of which a catalyzate is obtained containing 38-40% of aromatics, 13-15% of unsaturated hydrocarbons, and 31% of dimethylcyclopentanes. The presence has been detected also of small amounts of hexane isomers, methylcyclopentane, and high-boiling saturated hydrocarbons, the structure of which we have not yet succeeded in establishing.

The catalytic reactions of 4-methylcyclohexene may be diagrammatically represented as follows (the percentages refer to the original hydrocarbon):

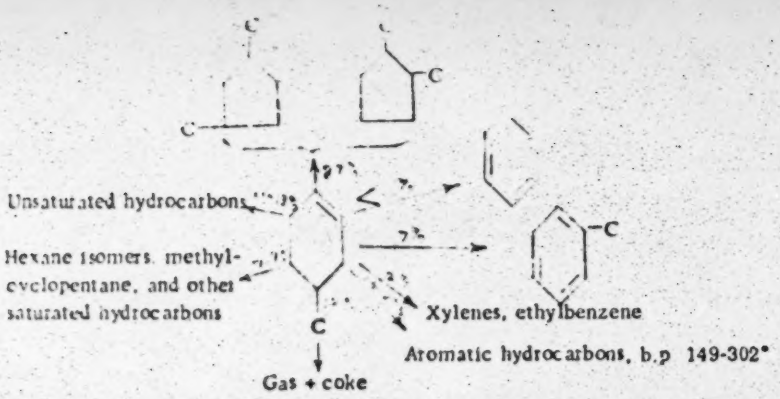


TABLE 8

Properties of Fractions of the Alkane-Cycloalkane Part of the 4-Methylcyclohexene Catalyzate

Fraction No	Boiling range (°C)	Amount (g)	Amount (% by wt.)	n_D^{20}	d_4^{20}	Aniline point
I	50 - 87.2	2.2	14.5	1.3892	0.7302	68.2
II	87.2 - 92.5	5.7	37.5	1.4082	0.7460	46.4
III	92.5 - 102.0	4.9	32.3	1.4155	0.7702	39.0
IV	102.0 - 142.0	1.5	9.9	1.4273	0.7722	45.0
V	142.0 - 228	0.7	4.7	1.4320	—	69.2
	Residue	0.2	1.1	—	—	—

Catalytic reactions of 1-octene.

1-Octene was passed over the same clay under the same conditions in portions of 100 ml. The results of the experiments are presented in Table 10.

The light hydrocarbons formed (boiling below 20°) were separated into three parts. The proportions by volume of these parts and their approximate compositions are given in Table 11.

Thus, 1-octene in contact with activated Troshkov clay undergoes a considerable amount of cracking (3% of gaseous hydrocarbons and coke). It was found that the approximate volume relationship of the components was $C_1 + C_2 : C_3 : C_4 = 1.3 : 3.9 : 1.6$, and 70-75% of these gases were unsaturated hydrocarbons.

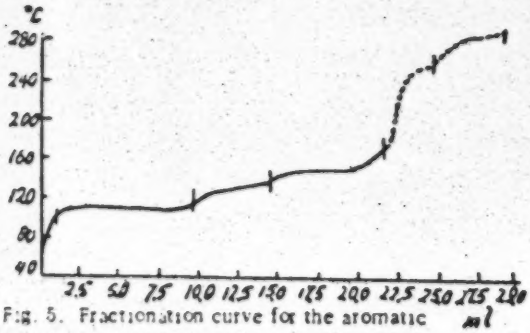


Fig. 5. Fractionation curve for the aromatic and unsaturated hydrocarbons in the methylcyclohexene catalyzate.

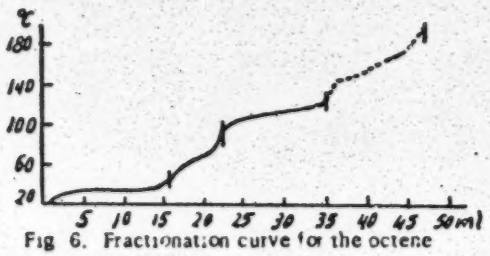


Fig 6. Fractionation curve for the octene catalyzate.

TABLE 9

Properties of Fractions Obtained from Aromatic and Unsaturated Hydrocarbons of the 4 Methylcyclohexene Catalyzate

Fraction No	Boiling range (°C)	Amount (g)	Amount (% by weight)	n_D^{20}	d_4^{20}	Iodine No.
I	50.0 - 100.0	0.7	2.8	1.3982	—	255.0
II	100.0 - 121.0	7.5	30.1	1.4860	0.8470	63.0
III	121.0 - 148.2	4.1	16.5	1.4840	0.8460	39.5
IV	148.2 - 170.0	6.0	24.1	1.4910	0.8681	6.8
V	170.0 - 200.0	2.7	10.8	1.5210	0.8703	Unsaturated
VI	200.0 - 292.0	3.6	14.4	1.5040	0.8794	absent
	Residue	0.3	1.3	—	—	

TABLE 10
Properties of Catalyzates from 1-Octene

Expt. No.	Yield				n_D^{20}	d_4^{20}	Sulfonatables (% by vol.)	Iodine No.
	Of liquid catalyzate		of gas condensed in trap (−60-70°)					
	(g)	(% by wt. of octene passed)	(g)	(% by wt. of octene passed)				
1	41.7	57.9	28.0	38.9	1.4100	0.7011	60.0	98.1
2	45.9	63.8	24.4	33.9	1.4115	0.7029	55.0	101.1
3	43.8	60.8	26.0	36.2	1.4160	0.7017	62.0	96.0
4	45.2	62.8	20.5	28.5	1.4135			
Mean	44.7	61.3	24.5	34.4	—	—	—	—

The united liquid catalyzate from two successive experiments (50 ml, i.e. 35.2 g) was fractionated through an efficient column into narrow fractions. Their properties are given in Table 12. The fractionation curve for the catalyzate is given in Fig. 6.

On the basis of the results given in Table 12 we may draw the following conclusions concerning the compositions of the various fractions:

Fraction I, boiling range 24.5-51.0°, consisted of a mixture of unsaturated and saturated C_8 hydrocarbons.

Fraction II, boiling range 51.0-100.0°, consisted of 32% of unsaturated C_8 and C_7 hydrocarbons, 30% aromatic hydrocarbons (mainly benzene), and 38% of saturated hydrocarbons.

Fraction III boiling range 100.0-124.0°, consisted of 26% of toluene, 11% of unsaturated, and 63% of saturated hydrocarbons.

Fraction IV, boiling range 124.0-197°, consisted mainly of aromatic hydrocarbons: it had a high refraction and a high content of sulfonatables. The content of unsaturated hydrocarbons, according to the iodine number, was 14%. The fraction, therefore, contained 81% of the aromatic hydrocarbons.

In order to make a more detailed analysis of the hydrocarbon composition, the united catalyzate from the first two experiments was separated by the adsorption method into an alkane-cycloalkane part and a mixture of aromatic and unsaturated hydrocarbons. The amount taken for the adsorption treatment was 60 ml (42.5 g). The fractionation curves of the two parts of the catalyzate are shown in Fig. 7 and 8.

TABLE 11
Composition of Gas Formed by the Cracking of 1-Octene

Expt. No.	Gas from system after trap (at −60-70°)				Gas from trap at −8°			Gas from trap and catalyzate at room temperature		
	Amount (liters at STP)	Group composition (%)			Amount (liters at STP)	Group composition (%)		Amt. (liters at STP)	Group composition (%)	
		Unsaturated hydrocarbons	Alkanes	Hydrogen		Unsaturated hydrocarbons	Alkanes		Unsat. hydrocarbons	Alkanes
1	2.70	70.8	28.0	1.2	8.11	80.0	20.0	3.2	69.2	30.8
2	2.98	65.8	30.9	3.3	7.93	68.2	31.8	2.8	81.3	18.6
3	2.23	75.9	24.1	none	7.23	75.3	24.7	3.8	73.1	26.9
4	2.62	69.0	31.0	none	7.81	72.8	27.2	3.0	72.8	27.2
Mean	2.63	70.4	28.5	1.1	7.8	74.1	25.9	3.2	74.1	25.9
Composition	—	Ethylene	Ethane, methane	Hydrogen	—	Propene	Propane	—	Butenes, isobutene	Butane, isobutane

The properties of the fractions separated from the alkane-cycloalkane part of the catalyzate are given in Table 13.

On the basis of the fractionation curve and of the properties of the fractions obtained we can state that

Fraction I consists essentially of n-pentane and isopentane; hexane, heptane and their isomers may be present in Fraction II, and in Fraction III—octane, its isomers, and hydrocarbons of more complex structure.

TABLE 12

Properties of the Fractions Obtained from the 1-Octene Catalyzate

Fraction No.	Boiling range (°C)	Amount (g)	Amount (wt.%)	n_D^{20}	d_4^{20}	Sulfonatable hydrocarbons (% by wt.)	Iodine No.	Unsaturated hydrocarbons (% by wt.)	Aromatic hydrocarbons (% by wt.)	Composition of aromatic hydrocarbons
I	24.5-51.0	10.0	29.1	1.3795	0.6481	63.0	232.5	64	–	–
II	51.0-100.0	4.6	13.4	1.4175	0.7127	62.0	89.4	32	30	Mainly benzene
III	100.0-124.0	11.2	32.6	1.4295	0.7312	37.0	25.1	11	26	Mainly toluene
IV	124.0-197.0	7.7	22.4	1.4980	0.8598	95.0	24.1	14	81	Higher aromatics
	Residue	0.0	2.5	–	–	–	–	–	–	–

TABLE 13

Properties of Fractions of the Alkane–Cycloalkane Part of the 1-Octene Catalyzate

Fraction No	Boiling range (°C)	Amount (g)	Amount (% by wt.)	n_D^{20}	d_4^{20}	Aniline point
I	28.0- 38.2	3.4	25.0	1.3568	0.6253	–
II	38.2-100.0	2.3	17.0	1.3790	0.6610	71.7
III	100.0-146.2	7.7	56.5	1.4010	0.7162	70.8
	Residue	0.2	1.5	–	–	–

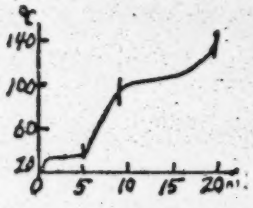


Fig. 7. Fractionation curve for the alkane-cycloalkane part of the octene catalyzate.

TABLE 14

Properties of Fractions Isolated from the Mixture of Aromatic and Unsaturated Hydrocarbons in the 1-Octene Catalyzate

Fraction No	Boiling range (°C)	Amount (g)	Amount (% by wt)	n_D^{20}	d_4^{20}
I	30 - 56.3	6.5	27.8	1.3800	0.6472
II	56.3-100.0	1.8	7.7	1.4218	0.7212
III	100.0-133.8	9.8	41.9	1.4633	0.7832
IV	133.8-190.0	5.0	21.7	1.4992	0.8611
	Residue	0.3	0.9	–	–

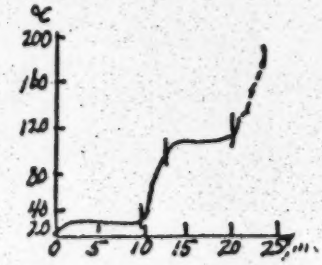
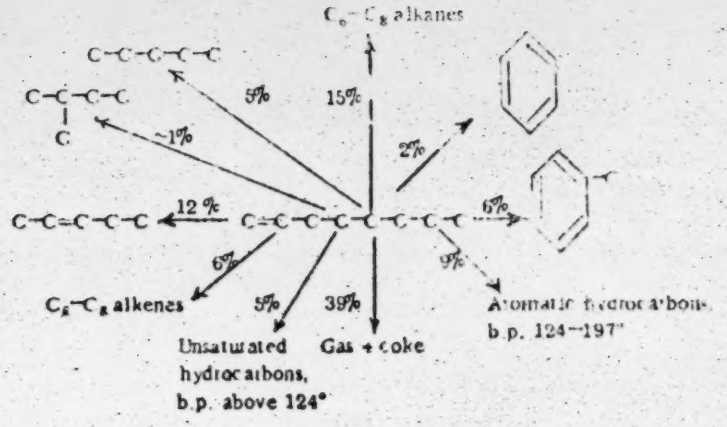


Fig. 8. Fractionation curve for the aromatic and unsaturated hydrocarbons of the octene catalyzate.

The properties of the fractions obtained from the mixture of aromatic and unsaturated hydrocarbons in the catalyzate are given in Table 14.

The fractionation curve and the properties show that Fraction I consisted mainly of 2-pentene, Fraction II evidently of hexene and heptene isomers and a small amount of benzene, Fraction III of toluene and probably of heptene and octene isomers, and Fraction IV of higher aromatics and high-boiling unsaturated hydrocarbons. Hence, the liquid catalyzate contained about 28% of aromatic hydrocarbons (including 4% of benzene, 9% of toluene, and about 15% of higher benzene homologs). The unsaturated hydrocarbons (32-34%) consisted of 2-pentene and evidently also, hexene, heptene, and octene isomers, and higher-boiling hydrocarbons. The saturated part of the catalyzate consisted of n-pentane (27%), a small amount of isopentane, and probably hexane, heptane, and octane isomers.

The results, after recalculation in terms of the original 1-octene, may be presented diagrammatically as follows:



SUMMARY

1. A study has been made of the reactions of cyclohexene, 4-methylcyclohexene, and 1-octene in presence of activated Troshkov clay at 450°.

2. It has been found that the catalytic treatment leads to redistribution of hydrogen with formation of aromatic and unsaturated hydrocarbons; at the same time partial isomerization of the cyclohexenes occurs with contraction of the ring to give five-membered cycles.

3. It has been established that the formation of aromatic hydrocarbons from cyclohexenes is accompanied by alkylation reactions.

4. It has been shown that under the conditions used 1-octene undergoes dehydrocyclization with formation of aromatic hydrocarbons.

5. Under the conditions investigated, cyclohexene, 4-methylcyclohexene, and 1-octene undergo partial cracking, and some of the decomposition products of octene undergo isomerization.

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PREPARATION OF 1,2-DIALKYLCYCLOALKANES

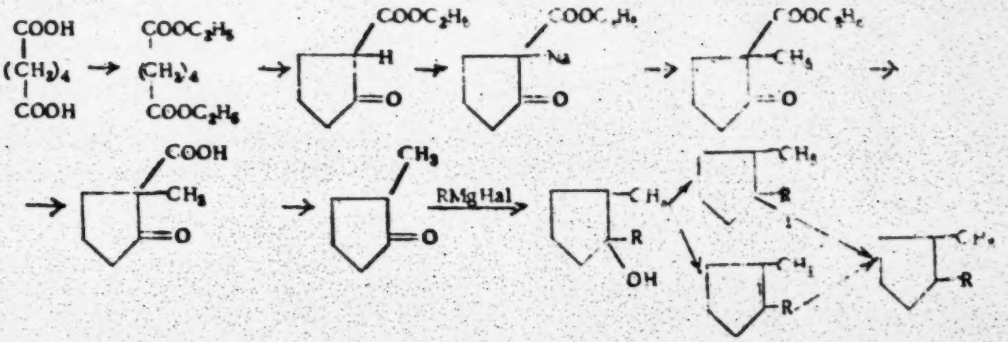
SYNTHESIS OF THE STEREOISOMERIC 1-BUTYL-2-METHYLCYCLOPENTANES

A. F. Plate, A. L. Liberman, and N. A. Momma

The preparation of dialkylcyclopentanes and dialkylcyclohexanes presents a rather difficult and laborious problem, but, since petroleum fractions contain naphthenic hydrocarbons in appreciable amount, a knowledge of the physical properties of these hydrocarbons is of great importance. In particular, in order to make a detailed study of the chemical composition of gasolines by the Raman-spectrum method [1], it is necessary to study the Raman spectra of these hydrocarbons, and for this purpose the hydrocarbons must be obtained by methods that guarantee a high degree of purity, so that they may be used as standards. However, very few methods of preparative value for obtaining dialkylcycloalkanes, particularly 1,2-dialkylcycloalkanes, are known. Thus, 1,2-dialkylcyclohexanes are generally prepared from the corresponding aromatic hydrocarbons, which are not always available in the pure state. 1-alkyl-2-methylcyclohexanes may be prepared also from 2-methylcyclohexanone. The latter method, however, suffers from the disadvantage that commercial 2-methylcyclohexanone may contain a certain amount of isomeric methylcyclohexanones, for it is generally prepared from a commercial o-cresol that is not free from other cresols.

Dialkylcyclopentanes are generally prepared from the corresponding alkylcyclopentanones. The method of preparing alkylmethylcyclopentanes proposed by Kazansky, Koperina, and Zemskaya [2] is of particular interest: they start not with individual methylcyclopentanones, but with a mixture of isomers, and the separation of the 1,2- and 1,3-isomers is carried out at the cycloalkane stage with the aid of an efficient fractionation column.

The main method for the preparation of 1,2-dialkylcyclopentanes is that used by Zelinsky and Frzhevalsky [3] as long ago as 1905 for the preparation of 1,2-dimethylcyclopentane. It consists in the cyclization of diethyladipate by Bouveault's method, which yields the ethyl ester of 2-oxocyclopentanecarboxylic acid, followed by replacement of the active hydrogen atom by an alkyl group via the sodium derivative, hydrolysis, and decarboxylation. The 2-methylcyclopentanone so obtained is converted by reaction with alkylmagnesium halide into the tertiary alcohol, which is converted into the disubstituted cyclopentane in the usual way. The scheme of the reaction is as follows:



This method, in which the essential intermediate products are 2-alkylcyclopentanones, was later used to a considerable extent by Rysselberge [4] for the preparation of a number of 1,2-disubstituted cyclopentanes, and, as a result, this method is sometimes erroneously referred to in the literature as Rysselberge's method. The preparation of 2-alkylcyclopentanes by this method involves several very laborious stages, and these substances are therefore not readily accessible, in spite of a number of improvements that have been introduced into the procedure [5].

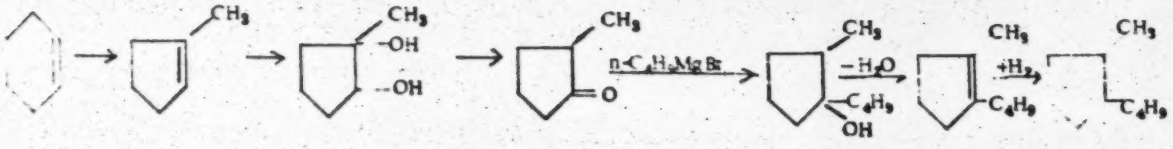
It appeared to us that a new method for the preparation of 2-methylcyclopentanone and 2-methylcyclohexanone might be found in the dehydration of secondary-tertiary diols: the dehydration of tertiary alcohol groups proceeds

much more readily than that of secondary alcohol groups, and it might be expected, therefore, that in this case, the corresponding enols would be formed as intermediate products, these then rearranging into ketones. Secondary-tertiary diols can be readily obtained by oxidation under defined conditions of accessible unsaturated cyclic hydrocarbons having a methyl group on a carbon at the end of a double bond. There are indications in the literature that heating of trans-1-methyl-1,2-cyclopentanediol with sulfuric acid yields 2-methylcyclopentanone [6]. It is true that Tiffeneau and Tchoubar [7] have shown that in the dehydration of trans-1-methyl-1,2-cyclohexanediol over a heterogeneous catalyst, for which purpose they used aluminum oxide, not only 2-methylcyclohexanone, but also its isomerization product, 1-methylcyclopentanecarboxaldehyde, is formed, but it might be expected that by the use of milder conditions for the dehydration of such diols this method of obtaining cyclic α-methyl ketones could be made satisfactory for preparative purposes.

1-Methylcyclopentene, being obtainable by the isomerization of cyclohexene by Zelinsky and Arbuzov's method, is now readily accessible. This hydrocarbon was oxidized at the double bond with a mixture of hydrogen peroxide and formic acid, yielding 1-methyl-1,2-cyclopentanediol, which when dehydrated in presence of iodine yielded 2-methylcyclopentanone in 70.7% yield, and the product formed by the loss of two molecules of water, methylcyclopentadiene, was formed simultaneously in 5% yield. By the use of this method for the synthesis of 2-methylcyclopentanone it is possible to avoid a number of laborious operations and to effect a considerable economy in time, as compared with Bouveault's method.

The results obtained for the dehydration of a secondary-tertiary diol, having a six-membered ring were different from those obtained for the dehydration of a five-membered diol. Dehydration of 1-methyl-1,2-cyclohexanediol in presence of an iodine crystal gave only a 42.3% yield of 2-methylcyclohexanone, which could be isolated only by vacuum distillation through a column of 20 theoretical plates. Together with 2-methylcyclohexanone, some methylcyclohexadiene was formed, and this, in order to prove its structure, was dehydrogenated and converted into toluene. An appreciable amount of an isomerization product of 2-methylcyclohexanone was formed also; the nature of this was not established. In the case of the six-membered ring therefore, dehydration of the diol cannot be used as a preparative method for obtaining 2-methylcyclohexanone.

2-Methylcyclopentanone, prepared as indicated above, was converted by reaction with butylmagnesium bromide into a tertiary alcohol, 1-butyl-2-methylcyclopentanol. On dehydration this gave 1-butyl-2-methylcyclopentene, which on hydrogenation yielded 1-butyl-2-methylcyclopentane, previously described by Denisenko and Frolova [9]. This hydrocarbon was resolved into its previously unknown stereoisomers by vacuum fractionation through a column of 80 theoretical plates. The synthesis of the 1-butyl-2-methylcyclopentanes was therefore carried out according to the scheme:



The constants of the stereoisomeric 1-butyl-2-methylcyclopentanes obtained in this investigation are given in Table 1, together with the properties of their lower homologs – 1,2-dimethylcyclopentanes, 1-ethyl-2-methylcyclopentanes, and 1-methyl-2-propylcyclopentanes – which were prepared and separated into cis-trans isomers by Chiurdoglu [10].

Of the two stereoisomers of 1-butyl-2-methylcyclopentane that we have prepared, the isomer having the lower constants and the higher molecular refraction must, according to the Auwers–Skita rule, be assigned the trans configuration. As will be seen from Table 1, with increase in the size of the radical the difference between the constants of the trans and cis isomers diminishes.

EXPERIMENTAL

Synthesis of 2-Methylcyclopentanone and 2-Methylcyclohexanone

1-Methylcyclopentene was prepared by the isomerization of cyclohexene over aluminum oxide [8] at 450°, the space rate being 0.4 volume of liquid over 1 volume of catalyst in one hour. The dried catalyzate was fractionated through a column of 45 theoretical plates and yielded 1-methylcyclopentene having the following constants: b.p. 74.2–75.2° (760 mm); n_D^{20} 1.4325; d_4^{20} 0.7821; found MR 27.27; calculated for C_6H_{10} MR 27.24. The

yield was 44-47%, calculated on the amount of cyclohexene passed, and about 54% on the amount of cyclohexene that reacted. Another isomer was obtained at the same time: 3-methylcyclopentene (b.p. 64-65° at 760 mm; n_D^{20} 1.4219, d_4^{20} 0.7654, found MR 27.26) in 15-16% yield on the amount of cyclohexene passed.

trans-1-Methyl-1,2-cyclopentanediol was obtained by the oxidation of 1-methylcyclopentene with a mixture of 30% hydrogen peroxide and 88% formic acid according to the procedure recommended for the oxidation of 1-methylcyclohexene [11], the only difference being that the temperature of the reaction mixture was maintained at 30-35°*; after removal of the solvent, the diol was distilled over under reduced pressure. Altogether, 371.2 g of 1-methyl-1,2-cyclopentanediol was obtained in the form of white crystals having the following constants: b.p. 93-95° (5 mm), m.p. 64.0-64.3°. The yield varied in different experiments from 62 to 66%. For trans-1-methyl-1,2-cyclopentanediol the literature [12] gives: b.p. 88-90° (1 mm); m.p. 65°. The preparation obtained distilled over at atmospheric pressure without decomposition or dehydration: b.p. 210-211° (760 mm).

TABLE 1

Hydrocarbon	Configuration	B.p. (°C/760 mm)	Δt	Refractive index	Δn	d_4^{20}	Δd	Mole. refraction	
								Found	Calculated
1,2-Dimethylcyclopentane	Trans	91.78	7.4	n_{He}^{20} 1.41203	0.01027	0.75137	0.02129	32.51	
	Cis	99.23		n_{He}^{20} 1.42230		0.77266		32.31	
1-Ethyl-2-methylcyclopentane	Trans	121.4-121.75	6.3	n_D^{20} 1.4220	0.0071	0.7696	0.0159	37.02	36.94
	Cis	127.7-128.0		n_D^{20} 1.4291		0.7846		36.85	
1-Methyl-2-propylcyclopentane	Trans	146.37-146.38	6.2	n_D^{20} 1.4274	0.00692	0.7774	0.0147	41.69	41.56
	Cis	152.58		n_D^{20} 1.4343		0.7921		41.49	
1-Butyl-2-methylcyclopentane	Trans	168.9-169.0 (751 mm)	5.6	n_D^{20} 1.4321	0.0060	0.7847	0.0133	46.37	46.18
	Cis	174.5 (751 mm)		n_D^{20} 1.4381		0.7980		46.15	

2-Methylcyclopentanone was obtained by the dehydration of 1-methyl-1,2-cyclopentanediol (371.0 g), which was heated with a crystal of iodine for 30 minutes in a Favorsky flask on a Babo funnel. The ketone formed was then distilled off slowly, separated from water, washed with sodium thiosulfate solution, with sodium carbonate solution, and with water, and then dried over potassium carbonate and distilled through a column of 20 theoretical plates at 100-115 mm pressure. The results of the distillation are given in Table 2.

Fraction III was a 2-methylcyclopentanone, obtained, after the distillation through the column, in 70.7% yield. It had the following properties: b.p. 138.7° (760 mm); n_D^{20} 1.4351; d_4^{20} 0.9197; found MR 27.85; calculated for $C_6H_{10}O$ MR 27.72. For 2-methylcyclopentanone the literature [13] gives: b.p. 138.4-138.5° (742 mm); n_D^{20} 1.4350; d_4^{20} 0.9191.

In order to identify the ketone obtained, its 2,4-dinitrophenylhydrazone was prepared. It melted at 154.3-154.8°; the 2,4-dinitrohydrazone of authentic 2-methylcyclopentanone melted at 154.0-154.7°, and in admixture these substances melted at 154.3-154.8°. According to the literature [6], the 2,4-dinitrophenylhyrazone of 2-methylcyclopentanone melts at 153-154°.

Fraction I resembled cyclopentadiene in odor and was evidently methylcyclopentadiene. This fraction, on being distilled at atmospheric pressure, yielded two main fractions:

Fraction A: b.p. 73-76° (747 mm); n_D^{20} 1.444, d_4^{20} 0.8147, found MR 26.14; calculated for C_6H_8 MR 26.77.

Fraction B: b.p. 138-160° (747 mm).

Fraction B evidently consisted mainly of a mixture of dimers of methylcyclopentadiene, whose rate of spontaneous polymerization is close to that of cyclopentadiene itself [14].

For methylcyclopentadienes of unknown structure, the literature [15] gives: b.p. 69-70° (736 mm); n_D^{18} 1.4460, d_4^{15} 0.8200, found MR 26.04; [14] b.p. 73° (760 mm), n_D^{20} 1.4509, d_4^{20} 0.8112. For the dimer of methylcyclopentadiene, the literature [14] gives: b.p. 98° (30 mm).

* In one experiment the temperature was raised during the oxidation to 45-48° with the result that partial esterification of the diol by formic acid occurred and a mixture boiling over a wide range (80-117°/5 mm) was obtained. After hydrolysis of this mixture with 5% alcoholic caustic soda, the pure diol was isolated.

1-Methylcyclohexanol was prepared from commercial cyclohexanone (730 g) purified via the bisulfite compound, and methylmagnesium iodide, prepared from 1055 g of methyl iodide. The synthesis was carried out in batches of 2.2-2.6 moles. The decomposition of the organomagnesium complex was effected by pouring the reaction mixture onto ice. The reaction product was worked up in the usual way, and after removal of ether, the residue was distilled from a Favorsky flask, when the distillate was found to solidify in the condenser. Yields of 62-70% were obtained. Altogether 553.6 g of 1-methylcyclohexanol (66.4% yield) was obtained; it had the following constants: b.p. 55.5-56.2° (9 mm), f.p. 25.9° (from cooling curve).

For 1-methylcyclohexanol, the literature [16] gives: b.p. 56.5° (10 mm), m.p. 26°.

TABLE 2

Fraction No.	B.p. (°C, p in mm Hg)	Amount (g)
I	Up to 78 (115)	12.8
II	78.0-81.0 (115)	3.7
III	81 (115), 78.4 (105)	221.5
IV	78.4-92.5 (102)	3.4
V	92.5-105.3 (103)	2.3
Residue	–	10.0
Losses	–	2.1

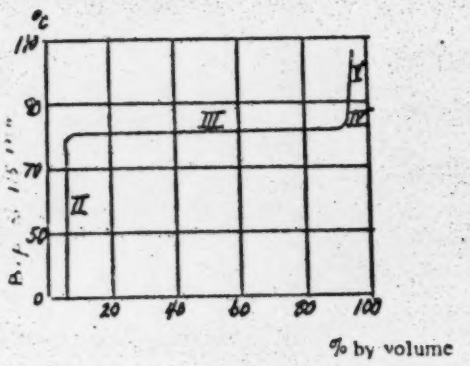


Fig. 1. Fractionation curve for 2-methylcyclopentanone

1-Methylcyclohexene was obtained by the dehydration of 1-methylcyclohexanol (519 g), which was effected by distilling it with iodine (2 g). The 1-methylcyclohexene obtained (422.7 g, 96.8%) had the following properties after being distilled through a column of 80 theoretical plates: b.p. 110.3-110.4° (760 mm), n_D^{20} 1.4510, d_4^{20} 0.8113; found MR 31.91; calculated for C_7H_{12}, MR 31.86.

The data in the literature for 1-methylcyclohexene are very contradictory [17].

1-Methyl-1,2-cyclohexanediol was obtained by the oxidation of 1-methylcyclohexene (292.5 g altogether) with a mixture of 29% hydrogen peroxide and 88% formic acid [11] at 30-35°. The yield of 1-methyl-1,2-cyclohexanediol was 266 g (72%); it had b.p. 123-127° (13 mm) and m.p. 80-81°. For trans-1-methyl-1,2-cyclohexanediol the literature gives m.p. 84° [12].

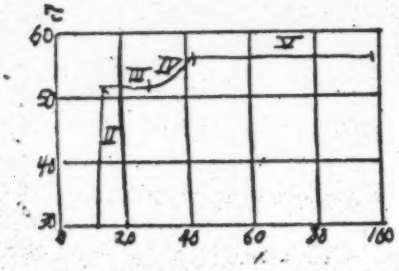


Fig. 2. Fractionation curve for dehydration product from trans-1-methyl-1,2-cyclohexanediol (fraction having b.p. 137-158° at 760 mm).

Dehydration of 1-methyl-1,2-cyclohexanediol. 1-Methyl-1,2-cyclohexanediol (282.7 g) and iodine (2.5 g) were introduced into a Favorsky flask. On being heated, the whole mass melted, and vigorous boiling then set in, water and substances not miscible with it coming over at 92-157° (measured in the vapor). The amount of water separating was 48 ml, whereas the amount calculated for the removal of one molecule of water was 39 ml. The reaction product, after being washed with sodium carbonate solution and then dried over potassium carbonate, was distilled from a Favorsky flask under atmospheric pressure. Up to 137° a fraction of 9.3 g (together with water) was collected, this was followed by 106.5 g of a fraction of b.p. 137-158°, and then decomposition set in with separation of water. The residue was vacuum-distilled, yielding a fraction which, on being redistilled came over at 70.0-71.5° (27 mm) (62.0 g).

The fraction boiling up to 137° yielded, after being dried and redistilled, a substance having the following constants: b.p. 108-113° (745 mm), n_D^{20} 1.4713; d_4^{20} 0.8352.

This substance, on dehydrogenation in presence of platinized charcoal, yielded toluene, which was converted into 2,4-dinitrotoluene, m.p. 69.0-69.7°. This preparation, in admixture with known 2,4-dinitrotoluene, m.p. 70.2-70.5°, melted at 69.4-69.7°. Thus, the head fraction obtained in the dehydration of 1-methyl-1,2-cyclohexanediol was evidently methylcyclohexadiene, the product of the removal of two molecules of water.

The properties of 1-methyl-1,3-cyclohexadiene have not been described in the literature. 2-methyl-1,3-cyclohexadiene, according to Zelinsky and Gorsky's results [18] has the properties: b.p. 110° (741 mm), n_D^{20} 1.4710, d_4^{20} 0.8292; and according to Horiuti, Otuki, and Okuda [19]: b.p. 110-111° (769 mm), n_D^{α} 1.4783, d_4^{0} 0.8451.

The fraction of b.p. 137-158° was vacuum-distilled through a column of 20 theoretical plates. The fractionation curve is given in Fig. 2. The following fractions were collected (Table 3):

TABLE 3

Fraction No.	B.p. (°C; p in mm Hg)	Amount (g)	n_D^{20}	d_4^{20}
I	Below 31 (20.5)	9.9	1.4750	0.8415
II	31 (20.5)-51.7 (17.5)	4.3	1.4512	0.7945
III	51.7 (17.5)-52.0 (18)	13.6	1.4389	0.9147
IV	52.0 (18)-56.1 (18)	13.2	1.4435	0.9151
V	56.1 (18) exactly	54.1	1.4481	0.9250
Residue	—	1.9	—	—
Losses	—	8.4	—	—

Fraction I was methylcyclohexadiene. Fraction III gave a 2,4-dinitrophenylhydrazone of m.p. 150.5-151°, the semicarbazone, which was obtained with difficulty and in low yield, melted at 165.4-166.4° (the bath was heated to 155° prior to the test). Fraction III did not decolorize bromine or cold permanganate solution, but decolorized warm permanganate solution immediately. No crystalline compound was obtained with dimedone. Schiff's reagent gave a feeble violet coloration to a layer of the organic substance. The nature of this fraction has not yet been established. Fraction V gave a 2,4-dinitrophenylhydrazone of m.p. 132.0-133.0°. The 2,4-dinitrophenylhydrazone of known 2-methylcyclohexanone melted, without being recrystallized, at 134.5-135.5°, and the two preparations in admixture melted at 134.0-134.5°.

Analysis of 2-methylcyclohexanone-1

Found %: C 74.55; 74.59; H 10.86; 10.86

$C_7H_{12}O$. Calculated %: C 74.95; H 10.78

The fraction of the dehydration product boiling at 70.0-71.5° came over almost completely at exactly 56.1° (18 mm) when distilled through the column. The amount collected at this temperature was 48.8 g, there were also a fraction (5.1 g) boiling at 56.1-57.5° (18 mm), a residue of 5.8 g, and losses amounting to 2.3g. The fraction of b.p. 56.1° (18 mm) had n_D^{20} 1.4481; d_4^{20} 0.9250; found MR 32.47; calculated for $C_7H_{12}O$ MR 32.34. This fraction, therefore, like Fraction V of the previous fractionation, was 2-methylcyclohexanone. The total yield of this substance was 102.9 g (42.3%).

The freezing point was determined on separate batches of 2-methylcyclohexanone by the cooling-curve method. The purest batch had a freezing point of −9.15°. For 2-methylcyclohexanone the literature [20] gives: b.p. 165.08° (760 mm), m.p. −14°; d_4^{20} 0.92500, [21]; n_D^{18} 1.4483.

Synthesis of 1-Butyl-2-methylcyclopentane, and its Separation into Cis and Trans Isomers

1-Butyl-2-methylcyclopentanol was prepared by the action of 2-methylcyclopentanone on butylmagnesium bromide. Owing to the fact that the ketone was not so readily accessible as butyl bromide, the latter was taken in 30% excess. The synthesis was carried out on batches of 0.5-1.0 mole. Altogether, 356.2 g of butyl bromide, 63.2 g of magnesium, and 196.0 g of 2-methylcyclopentanone were taken. The reaction mixture was treated in the usual way, and, after removal of ether, the reaction product was vacuum-distilled from a Favorsky flask. The results of the fractionation of one batch of the alcohol obtained are given in Table 4.

Fractions II-V were mixtures of the cis and trans isomers of 1-butyl-2-methylcyclopentanol, which explains their wide boiling ranges. An attempt to separate the stereoisomeric alcohols by distilling another batch through a column under a pressure of 6 mm was not successful: partial dehydration of the alcohol occurred. Constants were determined for two fractions of the alcohol obtained by repeated vacuum distillation:

Fraction A: b.p. 100.8° (16 mm); n_D^{20} 1.4563; d_4^{20} 0.8942; found MR 47.53.

Fraction B: b.p. 103.7-103.8° (16 mm); n_D^{20} 1.4576; d_4^{20} 0.8970; found MR 47.50; calculated for $C_{10}H_{20}O$ MR 47.70.

For 1-butyl-2-methylcyclopentanol (mixture of stereoisomers) the literature [9] gives: b.p. 101-102°

(6 mm) n_D^{20} 1.4560 d_4^{20} 0.8947 found MR 47.44.

Altogether, 148 g (54%) of 1-butyl-2-methylcyclopentanol was obtained.

1-Butyl-2-methylcyclopentene was obtained by dehydration of the alcohol in presence of iodine. The hydrocarbon obtained was distilled through a column of 20 theoretical plates. The results of the fractionation are given in Table 5.

TABLE 4

Fraction No	B.p. (°C, p in mm Hg)	Amount (g)	n_D^{20}
I	Up to 72 (12)	14.2	1.4362
II	72-86 (10)	17.8	1.4540
III	86-92 (12)	43.0	1.4558
IV	92-95 (13)	6.1	1.4575
V	95-98 (13)	17.0	1.4580
VI	98-108 (13)	10.0	1.4627

TABLE 5

Fraction No	B.p. (°C, p in mm Hg)	Amount (g)	n_D^{20}
I	71.0-88.9 (45.5)	14.3	1.4501
II	88.9 (45.5); 73.3-73.5 (22)	83.7	1.4515
III	73.5-74.0 (22)	1.1	--
Residue	--	3.6	--
Losses	--	4.0	--

Fraction II was pure 1-butyl-2-methylcyclopentene. A 70% yield of pure product was obtained: b.p. 169.7-170.0° (760 mm), n_D^{20} 1.4515; d_4^{20} 0.8109; found MR 45.94, calculated for $C_{10}H_{18}$ MR 45.71.

For 1-butyl-2-methylcyclopentene the literature [9] gives: b.p. 169.5-170.5° (752 mm), n_D^{20} 1.4480; d_4^{20} 0.8085, found MR 45.68.

1-Butyl-2-methylcyclopentane and its separation into cis and trans isomers. Hydrogenation of the cycloalkene was carried out in the cold without solvent in presence of platinized charcoal activated with palladous chloride [22]. The final purification of the 1-butyl-2-methylcyclohexane obtained was carried out by Tsvet's chromatographic adsorption method, silica gel being used as adsorbent. Altogether, 72.2 g (87%) of the hydrocarbon was obtained. In order to separate the cis and trans isomers the hydrocarbon was vacuum-distilled, using a manostat, through a column having a copper filling and of 80-plate efficiency. Two fractions were obtained, and these, on the basis of the Auwers-Skita rule, were assigned their configurations as cis and trans isomers. The yield of trans isomer (b.p. 74.0-74.1°/28 mm) was 53.3 g (74.8%), and that of the cis isomer (b.p. 78.7°/28 mm) was 14.1 g (19.8%); there was an intermediate fraction of 3.1 g (4.3%), and losses amounted to 0.8 g (1.1%). Neither a head nor a tail fraction was obtained although distillation was carried to dryness. The fractionation curve is given in Fig. 3. The boiling points of the stereoisomers at atmospheric pressure, and also their physical properties, are given above, in Table 1.

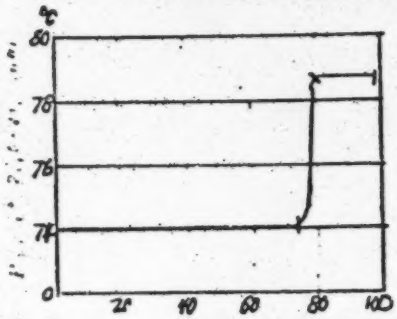


Fig. 3. Fractionation curve for 1-butyl-2-methylcyclopentane, with separation of cis and trans isomers.

Analysis of cis-1-butyl-1-methylcyclopentane:
Found %: C 85.84; 85.84, H 14.36; 14.16.

Analysis of trans-1-butyl-2-methylcyclopentane:
Found %: C 85.86, H 14.18
$C_{10}H_{20}$ Calculated %: C 85.63, H 14.37

SUMMARY

1. A suitable preparative method has been proposed for obtaining 2-methylcyclopentanone: it consists in the dehydration of the diol obtained by oxidizing 1-methylcyclopentene with a mixture of hydrogen peroxide and formic acid.

2. It has been shown that this method is of no value for the preparation of 2-methylcyclohexanone; in the case of the six-membered cycle, dehydration of the diol is accompanied by isomerization side reactions.

3. 1-Butyl 2-methylcyclopentane has been synthesized from 2-methylcyclopentanone prepared by the above method, and it has been separated into its cis and trans isomers.

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CATALYTIC OXIDATION OF THE SIMPLEST UNSATURATED HYDROCARBONS WITH HEAVY OXYGEN

L. Ya. Margolis and E. G. Plyshevskaya

A number of papers relating to the mechanism of the catalytic oxidation of hydrocarbons have recently appeared in the literature. Butyagin and Elovich [1] have established that there is a relation between the surface and space oxidation of propene in presence of platinum supported on barium sulfate. They showed that oxidation proceeds by two mechanisms: 1) purely surface, in absence of oxygen in the gas phase, and 2) surface – space. The succession of elementary processes is as follows: activated adsorption of oxygen, formation of a surface compound between propene and the oxygen of the catalyst, formation of a more highly oxidized intermediate compound, and then a fourth stage, which may proceed by the oxidation of this compound, either at the surface, giving CO_2 and H_2O, or in the space after desorption, giving CO_2 and H_2O. The authors could detect no trace of oxygen-containing products: aldehydes, and acids. Shalya, Piontkovskaya, and Polyakov [2], assert, in their paper on the mechanism of "mild" catalytic reaction, that all oxidative catalysts may yield products of partial oxidation under conditions favorable for the formation and preservation of these products. Increase in pressure and temperature leads to increase in the probability of the initiation of a homogeneous reaction at the platinum surface.

However, in numerous investigations on the oxidation of various hydrocarbons in presence of platinum catalysts [3], only traces of partial oxidation products have been detected in the reaction products: the process has always carried on to the final products, CO_2 and H_2O. Butyagin and Margolis [4], using Kovalsky's method of separation colorimetry, have established that at catalysts that produce severe oxidation (Pt, $MgCr_2O_4$) oxidation of hydrocarbons proceeds by a surface – space mechanism, but at mildly oxidative catalysts (V_2O_5, silver) a surface reaction occurs.

Thus the principal role in the formation of products of partial oxidation is assigned by some authors to a reaction that proceeds by a surface mechanism, a sharp distinction being made between mildly and severely oxidative catalysts; whereas on the other hand, other authors explain the formation of products of partial oxidation by the presence of a space-reaction stage. The use of labeled atoms O^{18} and C^{14} will make it possible to analyze the elementary stages of the oxidation process with greater certainty and to establish their role in the formation of oxygen-containing chain molecules. The present investigation is devoted to the elucidation of the part played by the oxygen of the catalyst and of the gas phase in the oxidation of a hydrocarbon in presence of various catalysts.

EXPERIMENTAL

Procedure. Oxidation of the hydrocarbons was carried out in the previously described apparatus [5] under static conditions and at low pressure (up to 2 mm Hg). Pure ethylene and propene gases were prepared by decomposition of alcohols over active Al_2O_3 and they were purified by repeated vacuum distillation. Oxygen (O^{16}) was prepared by decomposition of twice recrystallized potassium permanganate. Heavy oxygen (O^{18}) was prepared by the electrolysis of heavy oxygen water H_2O^{18}, containing 0.9% of O^{18}. Analysis of O^{18}-containing reaction products was carried out (as CO_2) by means of the mass spectrometer. The following were chosen as catalysts:

1) V_2O_5 (chemically pure), having a specific surface, determined by sorption of methanol, of 15 sq.m/g;

2) V_2O_4 obtained by reduction of V_2O_5, having a specific surface of 25 sq.m/g (its structure was checked by X-ray analysis: the parameters of the lattice were identical with those given in reference books);

3) $MgCr_2O_4$ (magnesium chromite), having a specific surface of 70 sq.m/g;

4) platinum supported on asbestos (2% Pt).

Oxidation of ethylene and propene. In a study of the reactions occurring in a mixture of ethylene and oxygen in presence of magnesium chromite, we have previously shown [6] that the hydrocarbon is sorbed at the surface of the catalyst, forming a stable compound, which can be removed from the surface by its further oxidation by the oxygen of the gas phase. The rate of oxidation of ethylene by the oxygen of the catalyst is considerably less than the rate of oxidation by oxygen of the gas phase.

When the balance of the reaction is analyzed, the oxidation process can be broken down into chemisorption and surface reaction. At magnesium chromite (see Table 1), as oxidation proceeds in a stoichiometric mixture of ethylene and oxygen, the proportion of the ethylene oxidized continuously falls, becoming 28% after five experiments, whereas the proportion of firmly sorbed ethylene at the surface increases from experiment to experiment, attaining the value of 66%. The surface of the catalyst is regenerated after treatment with oxygen, but the reaction products remain unchanged and consist of CO_2 and H_2O.

TABLE 1

Balance of the Oxidation Reaction in a Stoichiometric Mixture of Ethylene and Oxygen in Presence of Magnesium Chromite at 350°*

Expt No	Initial pressure of stoichiometric mixture**	Amount of ethylene (%)		
		Consumed in oxidation	Sorbed on surface	Residue
1	0.162	79.5	14.3	6.2
2	0.172	70.0	26.3	3.7
3	0.172	62.8	32.6	4.6
4	0.172	53.2	42.2	4.3
5	0.172	28.6	66.6	5.8
Oxygen (99 mm Hg) admitted				
6	0.163	78.0	21.0	1.0

* Duration of reaction 60 min. ** mm Hg.

TABLE 2

Balance of the Oxidation Reaction in a Stoichiometric Mixture of Ethylene and Oxygen in Presence of V_2O_5 at 430°

Expt. No.	Initial pressure of stoichiometric mixture*	Amount of ethylene (%)		
		Consumed in oxidation	Sorbed on surface	Residue
1	0.565	90.5	0.0	9.5
2	0.565	53.6	37.0	9.4
3	0.565	39.5	51.0	9.5
Treatment with oxygen				
4	0.560	67.0	25.0	8.0

* mm Hg.

Analysis of the balance of the oxidation reaction for a stoichiometric mixture of ethylene and oxygen in presence of vanadium pentoxide (see Table 2) enables us to assert that the surface of the catalyst undergoes considerable change in the course of the oxidation reaction. Thus, in the first experiment the proportion of the ethylene oxidized was 90%, but in the third it was only 9.5%. At the same time the proportion of ethylene adsorbed rose to 51%. Treatment of the catalyst surface with oxygen purified it from any compounds formed between ethylene and the oxygen of the catalyst. In Table 3 the results are given for the oxidation of the mixture $C_2H_4 + O_2$ in presence of V_2O_5 at various temperatures. With increase in temperature from 360° to 430°, the proportion of surface oxidation of C_2H_4 at the expense of the oxygen of the catalyst rose from 11 to 42%, i.e., the rate of the reaction of surface oxidation rose in comparison with the rate of oxidation by oxygen of the gas phase.

TABLE 3

Balance of the Oxidation Reaction of the Mixture $C_2H_4 + 3O_2$ in Presence of V_2O_5 at Various Temperatures*

Expt. No.	Initial pressure of mixture (mm Hg)	Temperature (°C)	Amount of oxygen (%)			Proportion of surface reaction (%)
			Used for oxidation	Adsorbed	Unused residue	
69	0.554	360	79.4	18.1	2.5	11.4
70	0.540	402	67.6	19.5	12.3	22.4
71	0.540	430	53.7	37.0	9.3	42.3

* Duration of reaction 30 min.

In the reaction products, in addition to CO_2, a large amount of CO was noted. It was established by special experiments that the appearance of carbon monoxide was associated with the decomposition of aldehydes.

in presence of O_2 under static conditions at low pressure and at 350-450°, yielding carbon monoxide and hydrogen or methane.

By the amount of CO formed, therefore, an estimate can be made of the amount of aldehydes formed; i.e., of the contribution made by the partial oxidation reaction in the over-all oxidation process.

From an analysis of the balance of the reaction of stage-wise oxidation of ethylene at a V_2O_5 surface covered with oxygen, it was possible to determine the proportions of the complete- and partial-oxidation reactions, and also the contribution made by irreversible chemisorption of ethylene. It was not found possible to measure the extent of the sorption of hydrocarbons by V_2O_5 since it proceeds practically instantaneously at 250-450° and at the same time surface oxidation by the oxygen of the catalyst occurs.

TABLE 4

Balance of Stage-wise Ethylene-Oxidation Reactions on V_2O_5 at Various Temperatures*

Expt. No.	Initial pressure of C_2H_4 (mm Hg)	Temperature (°C)	Amount of ethylene (%)				CO/CO_2 ratio
			Used in oxidation to CO_2	Used in oxidation to CO	Adsorbed	Residue	
68	0.500	360	11.3	55.2	6.5	27.7	4.9
70	0.516	402	16.3	64.0	8.4	9.7	3.9
71	0.520	430	16.7	66.2	9.0	8.1	3.9

*Duration of reaction 90 min.

TABLE 5

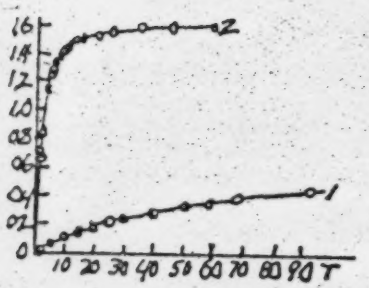
Balance of Stage-wise Ethylene-oxidation Reactions on V_2O_5 at Low Pressure and Various Temperatures

Expt. No.	Initial pressure of C_2H_4 (mm Hg)	Temperature (°C)	Amount of ethylene (%)				CO/CO_2 ratio
			Used in oxidation to CO_2	Used in oxidation to CO	Adsorbed	Residue	
68a	0.075	360	26.6	40.0	7.6	26.0	1.50
70a	0.080	402	31.5	48.7	9.0	8.7	1.54
71a	0.073	430	36.0	52.3	9.0	1.3	1.45

In Tables 4 and 5 are given the balances of the C_2H_4-oxidation reactions on V_2O_5 at various temperatures and initial pressures. With rise in temperature the proportion of unused ethylene falls, but the adsorption of ethylene on V_2O_5 is not great (6-9%). With rise in temperature the ratio CO/CO_2 falls; i.e., the rate of the complete combustion reaction rises. In Table 5 the results are given of the oxidation of C_2H_4 on V_2O_5 at low saturations of the surface with hydrocarbon. Comparison with the results at higher pressures shows clearly that the CO/CO_2 ratio in the reaction products falls; i.e., the proportion of the complete combustion reaction increases. The amount of oxygen on the surface and its concentration in the gas phase have, therefore, considerable effects on the direction of the oxidation reaction. In the figure, kinetic curves for the oxidation of propene on V_2O_5 and V_2O_4 are given. The rate of the oxidation of propene on V_2O_4 is considerably greater than that on V_2O_5.

Many investigators have noted [7] that for the oxidation of hydrocarbons the most active catalyst, at which a considerable amount of valuable oxygen-containing products is obtained, is V_2O_4. It has been shown in a number of investigations [8] that replacement of vanadium pentoxide by the lower oxide leads to increase in the yield of oxygen-containing products. By comparing the extents to which the oxygen of the catalyst participates in the oxidation of hydrocarbons for various catalysts, we may estimate the contributions made to the oxidative process by the surface stage, involving the oxygen of the catalyst, and by reaction at the expense of oxygen of the gas phase.

Oxidation of ethylene and propene by heavy oxygen. The study of the oxidation of hydrocarbons with the aid of the heavy oxygen isotope O^{18} was carried out by the above described procedure. Two series of experiments were carried out:



Kinetic curves for the oxidation of propene with oxygen at 400°: 1—on V_2O_5; 2—on V_2O_4.

a) A stoichiometric mixture of ethylene (or propene) and heavy oxygen (O^{18}) was heated in presence of a catalyst that did not contain this isotope; and

b) O^{18} was introduced into the catalyst, and the gas mixture consisted of hydrocarbon and O^{16}-oxygen.

Results of the analysis of the reaction products on the mass spectrometer are given in Table 6. The enrichment coefficient (in $CO^{16}O^{18}$ with respect to CO_2^{16}) was determined; natural carbon dioxide CO_2^{16} provided the standard unit of measurement and the enrichment coefficient of the original O^{18}-oxygen was 1.25 relative to this standard.

If the oxidation reaction proceeded only at the expense of the oxygen in the gas phase, then the enrichment coefficient for CO_2 would be unity; but for reaction of a stoichiometric mixture of ethylene or propene with oxygen in presence of V_2O_5 containing O^{18}, the enrichment coefficient was found to be 1.19 at 350° and 1.38 at 430°. Thus both the oxygen in the gas phase and that of the catalyst took part in the oxidation of the hydrocarbon.

TABLE 6

Oxidation of C_2H_4 and C_3H_6 with Heavy Oxygen in Presence of Various Catalysts

Expt. No.	Catalyst	Starting substances	Temperature (°C)	Enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$
2	V_2O_5 containing O^{18}	$C_2H_4 + 3O_2^{16}$	430	1.38
5	V_2O_5 not containing O^{18}	$C_2H_4 + 3O_2^{18}$	450	1.80
6	V_2O_5 not containing O^{18}	$C_2H_4 + 3O_2^{18}$	-	1.84
21	V_2O_5 containing O^{18}	$C_3H_6 + 4.5\ O_2^{16}$	350	1.19
23	V_2O_5 not containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.63
27	V_2O_5 not containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.66
24	V_2O_4 containing O^{18}	$C_3H_6 + 4.5\ O_2^{18}$	350	1.81

The extent to which the oxygen of the catalyst takes part in the oxidation process may be established by carrying out the inverse experiment: reaction of a mixture of hydrocarbon and heavy oxygen in presence of a catalyst not containing O^{18}. For the oxidation of ethylene or propene in presence of vanadium pentoxide, the extent to which the oxygen of the catalyst participated in the oxidation reaction was found to be about 30%. For V_2O_4 the proportion of the surface reaction was considerably greater. Results for the reaction of various mixtures of propene and oxygen in presence of V_2O_4 containing O^{18} are given in Table 7. For the oxidation of propene adsorbed on the catalyst (only O^{16}-oxygen being present in the gas phase), the rate of the surface reaction was low. As the oxygen concentration in the gas phase was reduced, the enrichment coefficient increased; i.e., the rate of the surface reaction increased in comparison with reaction at the expense of oxygen from the gas phase.

TABLE 7

Oxidation of C_3H_6 in Presence of V_2O_4 containing O^{18} with Various Amounts of Oxygen

Expt. No.	Catalyst	Initial composition of mixture (C_3H_6:O_2)	Temperature (°C)	Coefficient of enrichment $CO^{18}O^{16}/CO_2^{16}$	Notes
26	V_2O_4 containing O^{18}	Only oxygen in gas phase	350	1.26	C_3H_6 adsorbed on surface of catalyst.
24	V_2O_4 containing O^{18}	1:4.5	350	1.81	
27	V_2O_4 containing O_{18}	1:1	350	2.18	CO among reaction products. Enrichment coefficient of CO 2.36.

When the oxygen concentration in the gas phase was diminished, an appreciable amount of CO appeared in the reaction products, and this provided a measure of the extent of the partial oxidation reaction. The carbon monoxide was mixed with O_2^{18} and oxidized at a platinum wire to carbon dioxide, the enrichment coefficient of which was measured by means of the mass spectrometer. The enrichment coefficient $CO^{18}O^{18}/CO_2^{36}$ of the carbon dioxide so obtained was 2.35; i.e., the formation of carbon monoxide, and therefore of aldehydes, proceeded at the expense of the oxygen of the catalyst. In other words, the valuable oxygen-containing partial-oxidation products of hydrocarbons may be obtained in presence of those catalysts at which the rate of surface reaction is considerably greater than the rate of oxidation by oxygen from the gas phase. The enrichment coefficients of the reaction products obtained by oxidation of propene with heavy oxygen in presence of various catalysts are given in Table 8

TABLE 8

Oxidation of C_3H_6 with Heavy Oxygen at Various Catalysts not Containing O^{18}

No.	Catalyst	Starting substances	Temperature (°C)	Enrichment coefficient $CO^{18}O^{18}/CO_2$	Proportion of surface reaction (%)
1	V_2O_4	$C_3H_6 + 4.45\ O_2^{18}$	350	1.29	42.5
2	V_2O_3	$C_3H_6 + 4.5\ O_2^{18}$	350	1.66	29.6
3	$MgCr_2O_4$	$C_3H_6 + 4.5\ O_2^{18}$	350	1.77	25.0
4	Platinum on asbestos	$C_3H_6 + 4.5\ O_2^{18}$	280	2.36	0.0

The extent to which the oxygen of the catalyst took part in the oxidation reaction varied. At V_2O_4, for example, the proportion of surface reaction was 42%; at V_2O_3 it was 30%, and at platinum at 280° oxidation proceeded only in the gas space. Hence, as we have indicated in previous papers [4], a line may be drawn between catalysts of severe and mild oxidation. The formation of partial-oxidation products is associated with reactions that proceed by a surface mechanism.

Catalysts at which the rate of surface oxidation is high are evidently the most active mild-oxidation catalysts (V_2O_4).

Reduction of the oxygen concentration in the gas phase increases the proportion of surface oxidation at the expense of the oxygen of the catalyst and favors an increase in the yield of valuable oxygen-containing products. It will be obvious that macrokinetic factors (heat, diffusion) and unfavorable relations between the rates of oxidation of the hydrocarbons and of their oxygenic-containing derivatives will have a great effect on the yields of aldehydes and acids in presence of various mild-oxidation catalysts.

T. V. Sykova, undergraduate, took part in the investigation. In conclusion, I express my thanks to S. Z. Roginsky for valuable advice and constant interest in the work.

SUMMARY

1. A study has been made of the oxidation of ethylene and propene in presence of various catalysts (V_2O_5, V_2O_4, $MgCr_2O_4$).

2. By observations on the oxidation of ethylene and propene with heavy oxygen in presence of oxidative catalysts, the varying extents to which the oxygen of the catalyst participates in the process have been demonstrated.

3. A relation has been established between the formation of products of the partial oxidation of the hydrocarbons (aldehydes) and the extent to which the oxygen of the catalyst participates in the oxidation reaction.

4. The application of the mass spectrometer method of analysis to the reaction products from the catalytic oxidation of hydrocarbons has enabled us to explain the different mechanisms of the oxidation reactions at different catalysts.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 10. BEHAVIOR OF CYCLOHEXENE IN HYDROCONDENSATION CATALYSIS

Ya. Y. Eidus and N. I. Ershov

The catalytic hydrocondensation of carbon monoxide with olefins has been carried out only with α-olefins of the aliphatic series [1, 2], i.e., with ethylene and its nearest homologs propene, 1-butene, and isobutene, all of which readily undergo this reaction. It was necessary to determine the behavior in the hydrocondensation reaction with carbon monoxide of symmetrically disubstituted ethylene hydrocarbons, such as 2-butene. In order to solve this problem it was necessary to choose an olefin that could not isomerize into an α-olefin under the conditions of the reaction. Such an isomerization, with transfer of the double bond to the end of the molecule, is observed under the conditions of the oxo-synthesis reaction; i.e, the preparation of alcohols from olefins, H_2, and CO under pressure, the relevant examples being 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 2,4-dimethyl-2-pentene (as indicated by the nature of the reaction products) [3]. We chose cyclohexene, since its particular structure excludes the possibility of such isomerization. An α-olefin can be obtained from cyclohexene only by the opening of the stable six-membered ring, which is very improbable under the mild conditions of the hydrocondensation reaction (temperature, 190°; pressure, atmospheric).

EXPERIMENTAL

The apparatus and procedure were the same as in the previous investigations [1, 2]. The original cyclohexene was prepared in about 80% yield by dehydration of cyclohexanol (b.p. 158-161°/750 mm; d_4^{20} 0.9477) in presence of concentrated sulfuric acid by Coleman and Johnston's modification [6] of Sénderens' method [7]. In Experiments 218, 219, and 221 (Tables 1 and 2), the cyclohexene used was obtained in this way, and it boiled over the range 82-84° at 763 mm and had d_4^{20} 0.8106 and n_D^{20} 1.4468. The cyclohexene used in all the remaining experiments was distilled over through a column of 40 theoretical plates, at a single point of temperature, 82.0°/750 mm, and it had d_4^{20} 0.8104; n_D^{20} 1.4470; found MR 27.04, calculated for C_6H_{10} 27.19. The literature gives: d_4^{20} 83.19 at 760 mm; d_4^{20} 0.8107; n_D^{20} 1.4467 [8].

The cyclohexene passed to the glass catalysis tube (diameter 10 mm) from an automatic buret. All the experiments were performed at atmospheric pressure and at 190°. The liquid catalyzates obtained, which are described below, were dried over anhydrous copper sulfate, and the greater part of each was fractionated through a column having a metal single-helix filling, efficiency 40 theoretical plates. The residue from the fractionation was distilled from a small flask with Vigreux column (Favorsky flask).

TABLE 1

Expt. No.	Catalyst	Duration of expt. (hrs.)	Amount of cyclohexene passed		Volume of original gas (liters)	Space velocity (liters/liter-hr)			Amount of liquid catalyzate		Final volume of gas (liters)	Contraction of gas (%)
			ml	moles		cyclohexene	original gas	C_6H_{10} + gas	ml	(% of orig. C_6H_{10})		
218	46	14	111.5	1.09	0.0	0.18	–	39	109.4	98.2	–	–
219	47	16	137.8	1.35	47.0	0.25	84	138	132.0	95.8	28.7	39.0
220	48	10	115.0	1.13	33.5	0.33	95	157	112.0	97.4	17.7	47.2
221	49	20	140.5	1.39	50.2	0.20	74	120	138.2	98.4	28.25	44.0
222	48	23	230.7	2.20	66.0	0.28	82	142	229.0	99.3	34.0	48.5
223	50	27	112.4	1.07	42.9	0.12	45	71	119.6	106.5	19.7	54.1

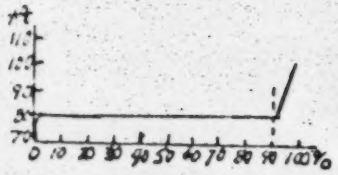


Fig. 1

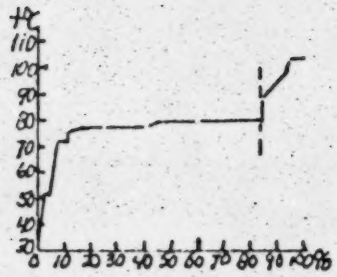


Fig. 2.

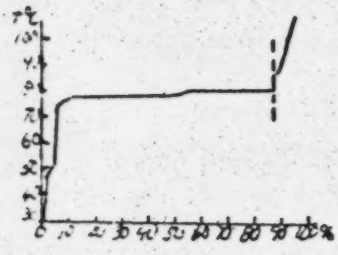


Fig. 3.

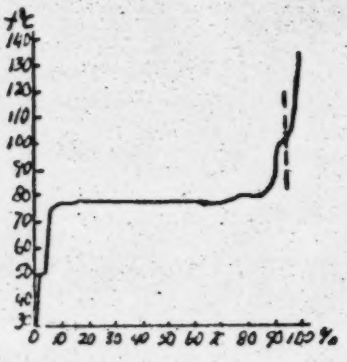


Fig. 4.

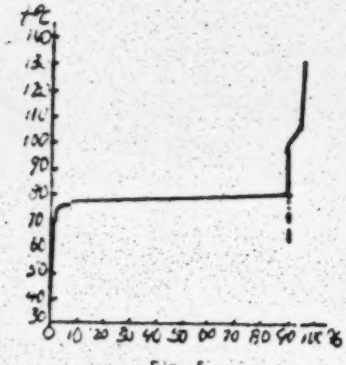


Fig. 5.

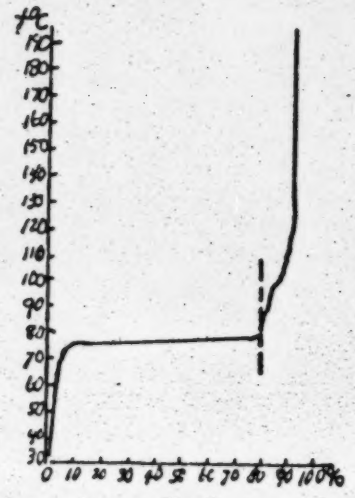


Fig. 6.

In Figures 1–6 the fractionation curves are given for the catalyzates, the parts on the left of the broken vertical line being the curves for fractionation through the column, and the parts on the right, fractionation curves for the residues distilled from Favorsky flasks.

Experiments with Cyclohexene without a Gas Carrier

Before investigating the behavior of cyclohexene in the reaction of hydrocondensation with carbon monoxide; i.e., before carrying out experiments with the ternary mixture C_6H_{10} – H_2 – CO, we studied the behavior of cyclohexene alone and also of the binary mixture C_6H_{10} – H_2 under similar conditions. The results obtained in the experiment on cyclohexene alone are given in Tables 1 and 2 (Expt. 218).

Cyclohexene was passed at a space velocity of 0.18 liters/liter-hour for 14 hours over freshly prepared catalyst (No. 46; weight 15.5 g, layer 44 cm in length). From 111.5 ml of hydrocarbon passed, 109.4 ml (98.2%) of liquid catalyzate was obtained; it had the constants d_4^{20} 0.8106; n_D^{20} 1.4470, which are not distinguishable from those of the original cyclohexene (see above). Distillation of 94 ml of the catalyzate through a column showed, however, that not all of the original hydrocarbon had been recovered unchanged. A fraction consisting of 91.3% by volume of the catalyzate came over in the range 71.5–72° (Fig. 1); the residue came over in the range 71.5–82° from a Favorsky flask. Details of the fractions obtained in the fractionation of the catalyzate from Expt. 218 – their volumes as percentages of the amount of catalyzate taken, their specific gravities, and their refractive indices – are given in Table 3 (intermediate fractions, comprising less than 0.2% of the original catalyzate, are not given in the table).

Experiments with Cyclohexene in a Current of Hydrogen

Two parallel experiments (Nos. 219 and 220, Tables 1 and 2) were carried out with cyclohexene passed in a current of hydrogen over freshly prepared catalyst (Nos. 47 and 48, each having weight of 15 g and layer of length 45 cm). In each pair of

TABLE 2

Expt. No.	Composition of original gas (% by volume)			Composition of original vapor phase (% by volume)				Composition of final gas (% by volume)				
	H_2	CO	C_2H_4	C_6H_{10}	H_2	CO	C_2H_4	H_2	CO	CO_2	C_nH_{2n+2}	C_nH_{2n}
218	–	–	–	100	–	–	–	–	–	–	–	–
219	100	–	–	40	60	–	–	95.0	–	–	5.0	–
220	100	–	–	43.5	56.5	–	–	Not determined				
221	88.6	11.4	–	38.3	54.7	7.0	–	75.1	–	0.9	24.0	–
222	89.4	10.6	–	42.7	51.2	6.1	–	98.8	–	–	1.2	–
223	63.9	7.0	29.1	35.8	41.0	4.5	18.7	47.7	0.2	0.5	51.3	0.3

values cited below, the first refers to Expt. No. 219 and the second to Expt. No. 220. Cyclohexene was passed for 16 (10) hours at a space velocity of 0.25 (0.33) liters/liter-hour. The space velocity of hydrogen was 84 (95) liters/liter-hour. The volume ratio C_6H_{10}: H_2 in the vapor-gas phase was 1:1.5 (1:1.3). The contraction of the hydrogen was 39.0% (47.2%). From 137.8 (115.0) ml of cyclohexene passed, 132 ml (95.8%) [112 ml (97.4%)] of liquid catalyzate was obtained.

TABLE 3
(p = 759 mm: Expt. No. 218)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	71.5-80.5	4.8	–	1.4488
II	80.5-81.5	12.0	0.8114	1.4480
III	81.5-82	74.5	0.8101	1.4465
IV	84 -98	6.5	0.8098	1.4470
V	98 -102	0.9	0.8110	1.4478
Residue	–	0.9	–	–
Original catalyzate	71.5-102	–	0.8106	1.4470

TABLE 4
(p = 744 mm: Expt. No. 219)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	38-56	5.2	0.7199	1.3992
II	62-72	5.4	0.7831	1.4330
III	75-77	34.2	0.7988	1.4394
IV	78-79.5	13.8	0.7876	1.4296
V	79.5-80	29.9	0.7808	1.4243
VI	80-98	9.0	0.7784	1.4255
VII	99-102	4.4	0.7821	1.4285
Residue	–	0.3	–	–
Original catalyzate	38-102	–	0.7832	1.4320

TABLE 5
(p = 750 mm: Expt. 220)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	32.5-56	4.7	0.7083	1.3960
II	73 -77.5	8.1	0.7855	1.4340
III	77.5-78	34.6	0.7915	1.4354
IV	79 -80	40.2	0.7852	1.4300
V	86 -108	7.4	0.7905	1.4370
Residue	–	0.5	–	–
Original catalyzate	32.5-108	–	0.7838	1.4320

The catalyzates, after being dried, had the constants d_4^{20} 0.7832, n_D^{20} 1.4340 and d_4^{20} 0.7838, n_D^{20} 1.4320. The dried catalyzates [105 ml (95 ml)] were fractionated through a column: 88.5% (87.6%) by volume of the catalyzate came over in the range 38-80° (32.5-80°) [Fig. 2 (Fig. 3)]. The residues were distilled over the range 80-102° (80°-108°) from Favorsky flasks.

The fractions, their amounts in per cent by volume, and their constants d_4^{20} and n_D^{20} are given in Tables 4 and 5.

Experiments with Cyclohexene in a Current of Hydrogen Mixed with Carbon Monoxide

Two parallel experiments were carried out also with cyclohexene; carried by a current of hydrogen mixed with carbon monoxide (Expt. No. 221 and 222, Tables 1 and 2). Expt. No. 221 was carried out with freshly prepared catalyst (No. 49, weight 15.5 g, layer 43 cm in length), whereas Expt. No. 222 was carried out with catalyst No. 48 after this had been used in Expt. No. 220. In each pair of values cited below, the first refers to Expt. No. 221, and the second to Expt. No. 222. The cyclohexene was passed for 20 (23) hours at a space velocity of 0.20 (0.28) l/l · hr. The space velocity of the gas mixture [11.4 CO: 88.6 H_2 (10.6 CO: 89.4 H_2)] was 74 (82) l/l · hr. The composition of the vapor phase was C_6H_{10} 38.3%, CO 7%, H_2 54.7% (C_6H_{10} 42.7%, CO 6.1%, H_2 51.2%). The total space velocity (vapor–gas phase) was 120 (142) l/l · hr. The contraction of the gas mixture (H_2 + CO) was 44% (48.5%). The composition of the final gas was CO_2 0.9%, H_2 75.1%,

CO 2.0%, C_nH_{2n+2} 24.0%, the ratio C_2H_6:CH_4 being 1:10 (Podbilnyak's analysis) (CO_2 0.0%, H_2 98.8%, CO 0.0%, C_nH_{2n+2} 1.2%). From 140.5 ml (230.7 ml) of cyclohexene passed, 132 ml (98.4%) [229.0 ml (99.3%)] was obtained of catalyzate having the constants (after being dried) of d_4^{20} 0.7972; n_D^{20} 1.4413 and d_4^{20} 0.8007; n_D^{20} 1.4440. The dried catalyzate [110 ml (202 ml)] were fractionated through a column: 89.6% (93.0%) by volume of the catalyzate came over in the range 35-100° (38-81°) [Fig. 4. (Fig. 5)]. The residue was distilled from a Favorsky flask over the range 102-152° (100-133°). The fractions, their amounts in per cent by volume, and their constants are given in Table 6 (Table 7).

Experiments with Cyclohexene in a Current of Hydrogen Mixed with Carbon Monoxide and Ethylene

It was of interest to investigate the effect of additions of ethylene to the ternary mixture C_6H_{10}–H_2–CO. Cyclohexene was passed in a current of the mixture H_2–CO–C_2H_4 over freshly reduced catalyst (No. 50; weight 18 g, layer of length 45 cm) for 27 hours at a space velocity of 0.12 1/1 hr (Expt. No. 223, Tables 1 and 2). The space velocity of the gas mixture (7 CO : 63.9 H_2 : 29.1 C_2H_4) was 45 1/1 hr, and its contraction was 54.1%. The composition of the vapor-gas phase was C_6H_{10} 35.8%, H_2 41.0%, CO 4.5%, C_2H_4 18.7%, and its space velocity was 71 1 1 hr. The composition of the final gas was H_2 47.7%, CO 0.2%, CO_2 0.5%, C_nH_{2n} 0.3%, C_nH_{2n+2} (mainly C_2H_6) 51.3%. From 112.4 ml of cyclohexene passed, 119.6 ml (106.5%) of liquid catalyzate was obtained; after being dried it had the constants d_4^{20} 0.8003; n_D^{20} 1.4422. The dried catalyzate (100 ml) was fractionated through a column and 80.8% by volume came over in the range 34.0-81.0° (Fig. 6). The residue was distilled from a 25-ml Favorsky flask over the range 84-150°, and the new residue from a 5-ml Wurtz flask. The fractions, their amounts in per cent by volumn, and their constants are given in Table 8.

TABLE 6
(p = 753, Expt. 221)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	35-72	5.5	0.7363	1.4011
II	73-76	8.6	0.8090	1.4514
III	77-78	52.8	0.8105	1.4504
IV	78-80	14.6	0.8137	1.4314
V	82-99	4.5	0.7756	1.4255
VI	99-100	3.6	0.7790	1.4330
VII	102-110	2.3	0.8170	1.4458
VIII	110-133	2.2	0.8028	1.4464
IX	133-152	0.4	—	—
Original catalyzate	35-152	—	0.7972	1.4413

Investigation of Reaction Products

It will be seen from Tables 1-8 and Figures 1-6 that the liquid catalyzates obtained in all of the experiments consist of three parts: 1) the higher-boiling part, 2) the middle part, represented on the fractionation curves as a plateau, and 3) the lower-boiling part.

1) Higher-boiling part of the catalyzate. The presence of Fractions IV and V (Table 3) shows that under the conditions of Expt. No. 218 products are formed that boil at a temperature higher than the boiling point of the original cyclohexene. They comprise 7.4% of the whole catalyzate and have a higher boiling limit of 102°. In Expt. No. 219-223 the products of boiling point higher than that of the original cyclohexene formed 7-14% of the catalyzate. In Expt. No. 219 and 220 with hydrogen as carrier, the upper boiling limits of the catalyzates were 102° and 108° respectively. When carbon monoxide was added (Expt. No. 219 and 220, the upper boiling limits were raised to 152° and 133° respectively, and the further addition of ethylene to the original mixture raised it to 195°. The higher-boiling products obtained from cyclohexene, CO and H_2 presented the greatest interest for investigation.

Fractions V-IX of Table 6 and Fraction VI of Table 7 were united. Part of this mixture (14 ml) having a boiling range of 95-145° and n_D^{20} 1.4390 was subjected to dehydrogenational catalysis (Zelinsky's method), two passages being given at a space velocity of 0.12 1/1 · hr in a current of hydrogen at 306-308° over a platinized charcoal catalyst prepared by Zelinsky's method [9]. The dehydrogenation catalyzate obtained had n_D^{20} 1.4862, a value that indicated a high content of aromatic hydrocarbons. Another part of the mixture (10 ml) was hydrogenated by means of two passages over the same catalyst in a current of hydrogen at 162-165°, and the catalyzate obtained had n_D^{20} 1.4239, close to the value (n_D^{20} 1.4230) for methylcyclohexane [8]. The hydrogenation catalyzate (5 ml) was now dehydrogenated over the same catalyst at 307° in a feeble current of hydrogen. The dehydrogenation catalyzate had n_D^{20} 1.4900, i.e., was strongly aromatic in character. The two dehydrogenation catalyzates (n_D^{20} 1.4862 and 1.4900) were united, and 16.5 ml of the mixture was fractionated (p = 754 mm) from a Favorsky flask into three fractions:

Fraction I, b.p. 95-105°; 4.4 ml; d_4^{20} 0.8458; n_D^{20} 1.4825

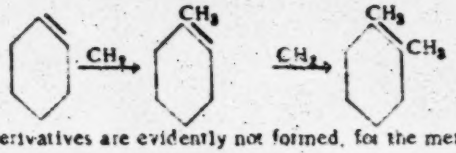
Fraction II, b.p. 105-118°; 10.2 ml; d_4^{20} 0.8516; n_D^{20} 1.4872

Fraction III, residue 1.7 ml; d_4^{20} 0.8542; n_D^{20} 1.4882

Fractions I and II gave a positive reaction for toluene when examined by Eidus and Fedichkina's test [10]. Fraction II was further fractionated, and the toluene fraction, b.p. 108-112°, was taken. A part of this (2.5 g) was subjected to Ullmann permanganate oxidation [11], and pure benzoic acid was obtained (m.p. 121.6°) with a yield of greater than 45%. In admixture with a pure preparation of benzoic acid it showed no depression in melting point.

It was thus shown that the main bulk of the higher-boiling fractions of the catalyzate obtained from the ternary mixture of cyclohexene, hydrogen, and carbon monoxide consisted of hydrocarbons having methylated six-membered rings. This indicates that methylation of cyclohexene proceeds in considerable measure under the conditions of Expt. No. 221 and 222. Fraction III (residue) (0.5 ml) was oxidized by the procedure of Norris and Vaala [12], and in the reaction product only phthalic acid could be detected (by a positive reaction, green fluorescence, with resorcinol). No isophthalic or terephthalic acid could be detected.

It has been shown, therefore, that in the hydrocondensation of cyclohexene with CO, 1,2-dimethyl-substituted products are formed according to the equation:



1,3- and 1,4-dimethyl derivatives are evidently not formed, for the methylene radical formed by reduction of CO unites with a carbon atom situated at the double bond.

2). Middle part of the catalyzate. The middle part of the catalyzate, which appears on the fractionation curves as a plateau, was found in all experiments to contain not only unchanged cyclohexene, but also cyclohexane and benzene. The middle part of the catalyzate obtained from the ternary mixture of cyclohexene, CO, and H_2 (Fractions II-V, Table 7) was investigated in the greatest detail. It was shown that these fractions consisted of

TABLE 7
(p = 757. Expt. 222)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig catalyzate)	d_4^{20}	n_D^{20}
I	38-56	1.5	0.7101	1.3970
II	72-75	4.8	0.7995	1.4464
III	76-78	31.5	0.8076	1.4485
IV	78.5-80	48.0	0.8036	1.4438
V	80-81	8.2	0.7955	1.4370
VI	100-133	5.0	0.8272	1.4392
Residue	—	0.4	—	—
Original catalyzate	38-133	—	0.8007	1.4440

TABLE 8
(p - 734. Expt. 223)

Fraction Number	Boiling range (°C)	Amt. (% by vol. of orig. catalyzate)	d_4^{20}	n_D^{20}
I	34-55	3.0	0.7024	—
II	66-75	6.5	0.7817	1.4380
III	76-76.5	17.3	0.8176	1.4554
IV	76.5-79	49.0	0.8079	1.4472
V	79.5-81	5.0	0.7945	1.4362
VII	84-95	3.0	0.7873	1.4338
VIII	98-150	10.0	0.7878	1.4333
	150-195	0.8	0.8064	1.4458
Original catalyzate	34-195	—	0.8003	1.4422

hydrocarbons having a six-membered ring, as well be seen from the following experiments. A mixture of Fractions II and III (Table 7) (10 ml) was given two passages in a current of hydrogen at 160-165° over a platinized charcoal catalyst. The catalyzate, after being dried over anhydrous copper sulfate, was found to be pure cyclohexane (n_D^{20} 1.4260). For cyclohexane the literature [8] gives: b.p. 80.8°, d_4^{20} 0.77867; n_D^{20} 1.4262 [8]

The hydrogenation catalyzate (8 ml) was further subjected to dehydrogenational catalysis, being passed over the same catalyst at 306° in a feeble current of hydrogen. The dehydrogenation catalyzate obtained had n_D^{20} 1.4918. Pure cyclohexane (3 ml) passed over fresh catalyst in order to determine its activity gave a catalyzate having n_D^{20} 1.4930. In a similar way 10 ml of a mixture of Fractions IV and V (Table 7) was hydrogenated under the same

conditions. The catalyzate obtained boiled at 80-81° and had n_D^{20} 1.4260, i.e. consisted of pure cyclohexane.

A mixture of fractions II, III, IV and V (Table 7) contained a considerable amount of benzene. A qualitative test was made for benzene by the method of Eidus and Fedichkina [10]. For this purpose the mixture (10 ml) was first treated with a methanol solution of mercuric acetate in order to bind cyclohexene (which interferes in the test for benzene) in the form of its compound with the mercuric salt [14], and the unchanged residue was distilled off under reduced pressure. The distillate, containing mainly benzene and cyclohexane, gave, after partial nitration, a positive reaction for benzene with powdered KOH (under petroleum ether): a yellow coloration with alkali [10].

The same mixture of fractions II, III, IV and V (Table 7) (n_D^{20} 1.4458) contained 33.2% by volume of cyclohexane (not absorbed by a mixture of sulfuric acid and phosphoric anhydride) and 54.3% of cyclohexene (Kaufmann bromine number of 107). The amount of benzene (by difference) was 12.5%. An artificially prepared mixture of the same composition had n_D^{20} 1.4456 and bromine number 98. 70% of its volume was absorbed by a mixture of sulfuric acid and phosphoric anhydride.

Since the conditions in all of our experiments (No. 218-223) were favorable for hydrogenation and unfavorable for dehydrogenation, it must be assumed that benzene may be formed under these conditions as a result of irreversible catalysis [15, 16] according to the equation:

$$3C_6H_{10} \longrightarrow C_6H_6 + 2C_6H_{12}.$$

A comparison of the ratio of benzene and cyclohexane in the mixture of fractions (II, III, IV and V, Table 7) with that indicated in the equation leads us to assume that a part of the cyclohexene is directly hydrogenated to cyclohexane by hydrogen contained in the original gas mixture.

The presence of benzene accounts also for the apparent inconsistencies observed between the boiling points on the one hand and the values of d_4^{20} and n_D^{20} on the other in the middle fractions of the catalyzates. Actually, fraction I (Table 3) has a somewhat higher n_D^{20} than the original cyclohexene, and fraction II has a somewhat lower boiling point and somewhat higher values of d_4^{20} and n_D^{20} than cyclohexene.

In Tables 4 and 5 fraction II boils lower than cyclohexene and cyclohexane, but has values of d_4^{20} and n_D^{20} that lie between those for these two hydrocarbons. The same can be said of fraction II of Table 5. Also, fraction III has much higher values of d_4^{20} and n_D^{20} than the following fraction IV. In Tables 6 and 7 fractions II and III also have values of n_D^{20} higher than that of fraction IV. In Table 8 fractions III, IV and V have values of d_4^{20} and n_D^{20} that rise as the boiling point of the fraction falls.

As already pointed out, all these relationships are to be explained by the presence of benzene. It was found, already in 1913 by Zelinsky and Aleksandrov [17], that benzene (b.p. 80.09° [8]) and cyclohexane (b.p. 80.8° [8]) form an azeotropic mixture boiling lower than its components (b.p. 77.5° [18], benzene content 55% by weight).

Also benzene forms an azeotropic mixture with cyclohexene, which according to some data [18] boils at 79.8° and has a benzene content of 85% by weight, and according to other data [19] boils at 79.45° and contains 84.5% of benzene. An azeotropic mixture of benzene and cyclohexane boiling at a lower temperature than its components must therefore have higher values of the constants d_4^{20} and n_D^{20} than cyclohexene. According to Pavlov [20], a mixture of the composition indicated has d_4^{20} 0.82504 and n_D^{20} 1.46155. In the fractionation benzene naturally occurs in the lower-boiling fractions, which must therefore have higher values of d_4^{20} and n_D^{20}.

In Expt. No. 218 on cyclohexene alone, the middle part of the condensate boiled over the range 80.5-82° and comprised 86.5% by volume of the catalyzate. In Expt. No. 219-223, the middle part of the catalyzate boiled over the range 77-81° and contained cyclohexene, cyclohexane, and benzene.

3) Lower-boiling part of the catalyzate. Fraction I (Table 3), boiling range 71-80.5°, formed 4.8% of the catalyzate, and, as will be seen from Fig. 1, the part of the catalyzate boiling below 77.5° formed less than 0.5% of the catalyzate and began to boil at 71.5°. Fractions I of Tables 4 and 5, boiling ranges 38-56° and 32.5-56°, formed 5.2% and 4.7% respectively of the catalyzates. From the catalyzate of Expt. No. 219 (Table 4) an intermediate fraction II was obtained (boiling range 62-72°, 5.4%). Fractions I of Tables 6 and 7: boiling ranges of 36-72° and 38-56° respectively, 5.5% and 1.5%. Fraction I (Table 8): 34-55°, 3%. Fraction II: 66-75°, 6.5%.

In Expt. No. 219-223, therefore, low-boiling fractions were obtained having a lower boiling limit of 32.5-38.0°. The least amount of such decomposition products was obtained in Expt. No. 222, which was carried out not

with freshly reduced catalyst, but with catalyst that had been in use for a long time. These fractions were not investigated more closely, but it will be seen from their constants and boiling ranges that they contain mainly aliphatic hydrocarbons. The small steps in the fractionation curves of Fig. 2 at 49-50° and 72° are notable: also the inflexions at 49-50° in the fractionation curves of Fig. 3 and 4. These temperatures correspond to cyclopentane (b.p. 49.2° [8]) and methylcyclopentane (b.p. 71.85° [8]).

Owing to the small amounts of these intermediate fractions, we could not carry out any work on the identification of these hydrocarbons, which could have been formed by isomerization accompanied by ring contraction from six- to five-membered and then demethylation. It is very probable that these hydrocarbons will be formed. Until recently such isomerization has been observed at temperatures much higher than 190° (over V_2O_3–Al_2O_3 at 400-500° [21], Al_2O_3, TiO_2, BeO, and silica gel at 400-450° [22], Al_2O_3–Fe_2O_3 at 300° [23], clay at 260° [24], SiO_2–Al_2O_3–ThO_2 [25]). Recently, however, formation of cyclopentane attributable to the isomerization of cyclohexane into methylcyclopentane and demethylation of the latter has been observed (at 200° over a Co catalyst in preparation of synthetic gasoline [26]).

SUMMARY

1. An investigation has been made of the application of the reaction of catalytic hydrocondensation of carbon monoxide with olefins to the case of cyclohexene.

2. It has been found that under the conditions of this process "irreversible-catalysis" reactions occur with formation of benzene and cyclohexane, hydrogenation into cyclohexane occurs, and also methylation occurs with formation of 1-methyl- and 1,2-dimethyl-substituted cyclohexene.

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ORGANOMAGNESIUM SYNTHESIS OF DIBUTYL-1-NAPHTHYLPHENYLSILANE, 1-NAPHTHYLTRI-p-TOLYLSILANE, TRIBENZYL-1-NAPHTHYLSILANE, AND BENZYL-1-NAPHTHYLPHENYL-p-TOLYLSILANE

V. S. Chugunov and A. D. Petrov

In the first two communications [1] we have described methods of synthesis of sila hydrocarbons containing 1-naphthyl radicals (which we were the first to prepare) both via organomagnesium compounds and via lithium compounds. We have shown that by the organomagnesium synthesis it is possible, with tetraethoxysilane as starting material, to attach not more than two of the sterically hindering radicals $1\text{-}C_{10}H_7$ to a silicon atom. It was established that tributyl-1-naphthylsilane and trihexyl-1-naphthylsilane are notable for their very low solidification points (of the order of −52° and −33°); also, the nonsymmetrical tetraarylsilane, 1-naphthyltriphenylsilane, melts at 183-185°, whereas tetraphenylsilane [2] melts at 234°.

Continuing these investigations, we have attempted to prepare 1-naphthyltrioctylsilane by the organomagnesium synthesis. However, under the conditions of synthesis (elevated temperature) this sila hydrocarbon was obtained only in admixture with 1-naphthyldioctylsilane. We have also prepared dibutyl-1-naphthylphenylsilane, a thick liquid having a specific gravity somewhat greater than unity and congealing to a glass at −5-7°. It has been found further that the melting point of 1-naphthyltri-p-tolylsilane (174°) is not very much lower than that of tetra-p-tolylsilane [3] (226°), and that the melting point of the isomeric tribenzyl-1-naphthylsilane is 54° (glass), which can evidently be related to the low melting point of tetrabenzylsilane [4] (127.5°). Finally, we have prepared the asymmetric sila hydrocarbon, benzyl-1-naphthylphenyl-p-tolylsilane and have found that this high-molecular-weight sila hydrocarbon, which contains five aromatic rings in its molecule, is a thick liquid at room temperature, a fact that can evidently be related to the high degree of asymmetry of its molecule.

EXPERIMENTAL

The syntheses of the sila hydrocarbons were in all cases performed via organomagnesium compounds. Decomposition of the organomagnesium complex and isolation of the final reaction products were carried out by Khotinsky and Seregenkov's method [5].

1. Dibutyl-1-naphthylphenylsilane. Diethoxy-1-naphthylphenylsilane (b.p. 365-370°; d_4^{20} 1.0552; n_D^{21} 1.5842), (20 g) and kerosene (saturated, b.p. 160-170°) (100 ml) were added to butylmagnesium chloride (0.2 mole), and the mixture, after removal of ether, was boiled in kerosene for three hours. Decomposition of the complex and fractionation of the product yielded 16.2 g of an oily liquid (b.p. 254-260°/20 mm), which, in order to remove impurities (substances containing ethoxyl groups), was again treated in kerosene at the boil with the same amount of butylmagnesium chloride. After being distilled twice, dibutyl-1-naphthylphenylsilane had the following constants: b.p. 256-260°/20 mm; d_4^{20} 1.258, n_D^{20} 1.5780; yield 29% based on the $1\text{-}C_{10}H_7C_6H_5Si(OC_2H_5)_2$ taken.

	Found %.	Si 8.1; 7.8
$C_{24}H_{32}Si$.	Calculated %:	Si 8.08

2. 1-Naphthyltrioctylsilane. Triethoxy-1-naphthylsilane (29 g) and kerosene of b.p. 160-170° (100 ml) were added to octylmagnesium bromide (0.25 mole), and after removal of ether the mixture was boiled in kerosene for four hours. Decomposition and fractionation yielded a fraction of b.p. 400-410° (14.8 g), which was again treated with excess of octylmagnesium bromide in kerosene at the boil for four hours. After two distillations a thick light-yellow oil was obtained in 27% yield; it had the following constants: b.p. 406-410°; d_4^{20} 0.9136; n_D^{20} 1.5272.

	Found %:	C 82.06; 81.91,	H 11.32, 11.35,	Si 6.86, 6.78
$C_{34}H_{56}Si$.	Calculated %:	C 82.65	H 11.79;	Si 5.68
$C_{26}H_{48}Si$.	Calculated %:	C 81.6;	H 11.66;	Si 7.35

As the results of the elementary analysis for carbon, hydrogen, and silicon did not correspond to the compounds cited above, in spite of the fact that the contents of these elements totaled to 100%, it was suggested that the substance obtained contained not only 1-naphthyltrioctylsilane, but also a sila hydrocarbon of lower molecular weight, which, under the conditions of the synthesis, could only be 1-naphthyldioctylsilane, the presence of which we demonstrated by the method proposed by Price [6]

The mixture to be analyzed (0.4422 g) was dissolved in acetone (30 ml) in a Tserevitinov apparatus, and to this solution an equal amount of a 20% solution of caustic potash was added. The volume of hydrogen obtained was 12.4 ml corresponding to 47.4% of 1-naphthyldioctylsilane Treatment of 0.2014 g of the mixture gave 6.5 ml of hydrogen corresponding to 45.2% of 1-naphthyldioctylsilane.

3 1-Naphthyltri-p-tolylsilane. To p-tolylmagnesium bromide, prepared from 6 g of magnesium in 200 ml of ether and 69 g of p-bromotoluene, 15 g of triethoxy-1-naphthylsilane and 100 ml of saturated kerosene, b.p. 160-170° were added After removal of ether, the mixture was boiled in kerosene for four hours, and the complex formed was then decomposed with 50% acetic acid. Fractionation yielded 126 g of an amber-colored liquid, b.p. 320-340° 30 mm which solidified to a glass at room temperature. In order to remove oxygen-containing compounds that were probably present as impurity, the product was again treated with an excess of p-tolylmagnesium bromide in boiling kerosene for four hours Two vacuum fractionations yielded 9.8 g of a glasslike product, which, after two crystallizations from benzene, was obtained in the form of fine colorless crystals, m.p. 174-176°. The yield was 20%, based on the triethoxy-1-naphthylsilane taken.

Found %: C 86.60, 86.57, H 6.57, 6.73; Si 6.68, 6.67
$C_{31}H_{28}Si$. Calculated %: C 86.90; H 6.55; Si 6.55

Found M 420.2, 416.6
$C_{31}H_{28}Si$. Calculated M 428.6

4. Tribenzyl-1-naphthylsilane. To benzylmagnesium chloride (0.25 mole), prepared from 32 g of benzyl chloride and 6 g of magnesium, 14.5 g of triethoxy-1-naphthylsilane and 100 g of kerosene were added. After removal of ether, the mixture was boiled in kerosene at 160-170° for four hours, after which the complex was decomposed A thick liquid, b.p. 310-318°/28 mm, was isolated, and this was then again treated with an excess of benzylmagnesium chloride After decomposition of the complex, the product was vacuum-distilled twice, yielding (at 314-318°/26 mm) 4.2 g (10% of triethoxy-1-naphthylsilane taken) of tribenzyl-1-naphthylsilane, which solidified to a clear glass, softening at 54-56°. The product distilled at atmospheric pressure without decomposition at 386-389°.

Found %: C 86.68; 86.86; H 6.73; 6.51; Si 6.18; 6.36
$C_{31}H_{28}Si$. Calculated %: C 86.90; H 6.55; Si 6.55

5. Benzyl-1-naphthylphenyl-p-tolylsilane. The synthesis of this asymmetric sila hydrocarbon was performed in the following stages:

a) Ethoxy-1-naphthylphenyl-p-tolylsilane. To p-tolylmagnesium bromide (0.1 mole), prepared from 2.4 g of magnesium, 200 ml of ether, and 17.1 g of p-bromotoluene, 32.5 g of diethoxy-1-naphthylphenylsilane (the constants of which are given above) and 100 ml of saturated kerosene were added. After removal of ether the mixture was boiled in kerosene at 160-170° for four hours, after which the complex was decomposed and the product was vacuum-distilled twice, yielding 22 g of ethoxy-1-naphthylphenyl-p-tolylsilane, b.p. 310-318°/80 mm) and d_4^{20} 1.225, as a thick, oily liquid.

Found %: Si 7.65; 7.03
$C_{25}H_{24}SiO$. Calculated %: Si 7.69

b) Benzyl-1-naphthylphenyl-p-tolylsilane. Ethoxy-1-naphthylphenyl-p-tolylsilane (20 g) and kerosene of b.p. 160-170° (100 ml) were added to the product obtained from 17.1 g of benzyl chloride, 2.4 g of magnesium, and 200 g of ether. After removal of ether, the mixture was boiled in kerosene for four hours, and the product obtained by decomposing the complex was vacuum-distilled, yielding 8 g of benzyl-1-naphthylphenyl-p-tolylsilane, having the following properties: b.p. 306-310°/30 mm, d_4^{20} 1.126, softening point + 40-45°.

Found %: C 87.04, 87.15; H 5.96; 5.92; Si 7.4
$C_{30}H_{26}Si$. Calculated %: C 87.2; H 5.7 Si 7.0

SUMMARY

1. It has been confirmed that tetraarylsilanes of unsymmetrical structure, like their tetraarylmethane analogs, melt at lower temperatures than those of symmetrical structure.

2. It has been shown that, with increase in the chain length of the alkyl (up to C_8H_{17}) in the organomagnesium synthesis of compounds of the type $1\text{-}C_{10}H_7SiR_3$ at elevated temperatures, in addition to 1-naphtyltrioctylsilane, $1\text{-}C_{10}H_7SiH(C_8H_{17})_2$ is formed.

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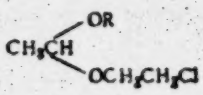
REACTIONS OF VINYL ETHERS

CHEMICAL PROPERTIES OF ALKYL 2-CHLOROETHYL ACETALS

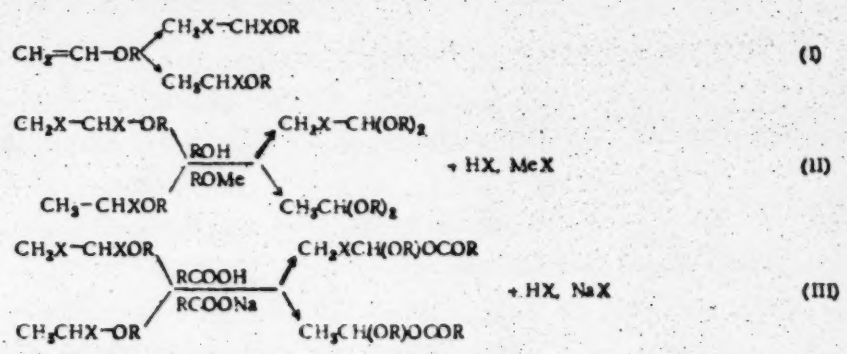
M. F. Shostakovsky and N. A. Gershtein

This investigation was devoted to the question of the mobility of the chlorine and hydrogen atoms occurring respectively in the 2- and 1-positions in the chloroethyl group of alkyl 2-chloroethyl acetals of general formula



The question of the mobility of 1-halogen and 2-hydrogen has received much study in the reactions of halogen addition and hydrogen halide addition to alkyl vinyl ethers, and it has been considered in papers by Shostakovsky, Sidelkovskaya, and Bogdanova [1, 2, 3].

These authors have shown that 1-halogen in the products of the addition of halogen and of hydrogen halide to alkyl vinyl ethers is exceptionally mobile and is readily quantitatively titrated by the Volhard method and with alkali, and is also readily replaced by alkoxyl and acyl groups:

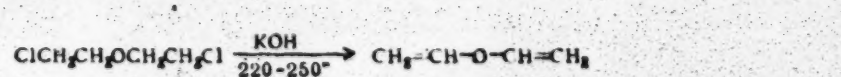


(X being halogen)

At the same time it was noted that 2-hydrogen was very mobile in alkyl 1,2-dihaloethyl ethers, which was shown by the tendency for hydrogen halide to be eliminated from these in presence of tertiary amines, with formation of 2-halovinyl ethers [4]:

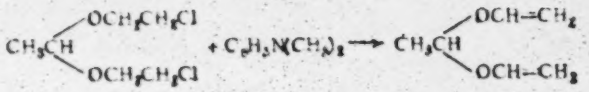
(R being alkyl)

The exceptionally high mobility of 1-halogen, and also the great readiness with which elimination and replacement reactions occur, as compared with the corresponding reactions of halogenated hydrocarbons [5], is to be attributed mainly to the effect of the ether oxygen atom, which has a free pair of electrons. Gulyaeva and Dauguleva [6] have shown, however, that in the analogous groupings of "Chlorex" $(ClCH_2CH_2)_2O$ the elimination of HCl with loss of the 2-halogen requires extremely severe conditions, divinyl ether being obtained in very low yield:



We have now made an examination of the mobility of 2-halogen and 1-hydrogen in alkyl 2-chloroethyl acetals $[CH_3CH(OR)OCH_2CH_2Cl]$.

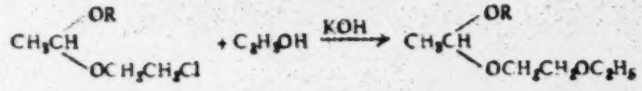
By the action of dimethylaniline on the bis(2-chloroethyl) acetal we did not, however, succeed in effecting the following reaction.



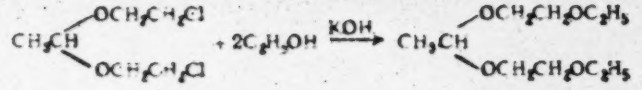
(V)

When acetaldehyde bis(2-chloroethyl) acetal was heated at 100° for 12 hours per day for three days with an excess of dimethylaniline, there was no precipitate, and no volatile products were formed and retained in the traps, which were cooled to −50°. Under these conditions neither elimination of hydrogen chloride nor replacement of halogen by an amine group occurred. When an ether solution of the bis(2-chloroethyl) acetal was heated at a feeble boil (40°) with powdered KOH for several hours, the bis(2-chloroethyl) acetal was recovered unchanged. By heating the acetal with liquid ammonia for 5-6 hours at 140-150°, we have succeeded in replacing chlorine by the amino group [7].

The replacement of chlorine by alkoxyl in mono- and bis-2-chloroethyl acetals proceeds comparatively readily when these substances are heated with alcoholic solutions of caustic potash. The alkoxy derivatives are formed in good yield and the method may be used for preparative purposes:



(VI)



(VII)

In this communication we describe the syntheses and properties of the 2-ethoxyethyl ethyl, the butyl 2-ethoxyethyl and the bis(2-ethoxyethyl) acetals of acetaldehyde. Only the preparation of the bis(2-ethoxyethyl) acetal is to be found in the literature: from acetaldehyde and Cellosolve by Adkins and Street [8]:

$$CH_3CHO + 2C_2H_5OCH_2CH_2OH \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2 + H_2O$$

and from acetylene and Cellosolve in presence of acid catalysts (BF_3 and HgO) by Nieuwland and coworkers [9]:

$$HC \equiv CH + 2HOCH_2CH_2OC_2H_5 \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2.$$

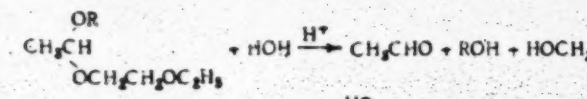
In the latter case the reaction evidently proceeds in two stages:

$$HC \equiv CH + HOCH_2CH_2OC_2H_5 \rightarrow CH_2{=}CH{-}O{-}CH_2CH_2OC_2H_5$$

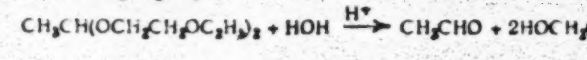
$$CH_2{=}CH{-}OCH_2CH_2OC_2H_5 + HOCH_2CH_2OC_2H_5 \rightarrow CH_3CH(OCH_2CH_2OC_2H_5)_2.$$

The 2-ethoxyethyl ethyl and butyl 2-ethoxyethyl acetals were obtained for the first time by us.

The structures of the synthesized acetals were proved by hydrolysis and quantitative estimation of acetaldehyde.



(VIII)



(IX)

EXPERIMENTAL*

Synthesis of the 2-Ethoxy Ethyl Acetal $CH_3CH(OC_2H_5)(OCH_2CH_2OC_2H_5)$

The original 2-chloroethyl ethyl acetal was prepared by the method described previously [10] and had the following constants: b.p. 23-23.8°/2 mm; d_4^{20} 1.0190; n_D^{20} 1.4216.

A solution of caustic potash (57 g) in absolute ethanol (480 g) was introduced into a three-necked round-bottomed flask provided with mercury-sealed stirrer, reflux condenser, thermometer, and dropping funnel. Acetaldehyde 2-chloroethyl ethyl acetal (77 g) was added from the dropping funnel over a period of 2 hours 30 minutes

* A. K. Gorban assisted in the experimental part.

at room temperature. No crystalline precipitate appeared in the cold, i.e., the reaction did not go at room temperature. The mixture was therefore heated with stirring at 80° for eight hours. The solution became brownish red and a white precipitate of potassium chloride appeared. The reaction mixture was filtered under suction and then distilled from a flask fitted with a Vigreux column. It was necessary on several occasions to interrupt the distillation in order to filter off precipitated potassium chloride.

On each occasion the precipitate of potassium chloride was washed with ether. In this way 36 g of potassium chloride (96.5% of the theoretical amount) was separated. The residue in the flask separated into layers. The lower layer was found to be an aqueous solution of caustic potash, and the upper was the reaction product, which was dried with potassium carbonate and vacuum-fractionated, yielding 9.5 g (11.7%) of the 2-ethoxyethyl ethyl acetal, b.p. 40-40.5°/4 mm, n_D^{20} 0.8955.

Found MR 44.33
$C_8H_{18}O_3$. Calculated MR 44.07

The substance obtained was a mobile clear liquid, very readily soluble in water, diethyl ether, ethanol, and benzene.

Found M: 148; 151.8
$C_8H_{18}O_3$. Calculated M: 162.2

Found %: C 58.61; 58.73; H 11.30; 11.18
$C_8H_{18}O_3$. Calculated %: C 59.23;
Purity %: 97.9, 99.7 (iodometrically)

Synthesis of the Butyl 2-Ethoxyethyl Acetal $CH_3CH(OC_4H_9)(OCH_2CH_2OC_2H_5)$

The butyl 2-chloroethyl acetal used for the reaction had b.p. 55-56°/2mm, d_4^{25} 0.9838; n_D^{20} 1.4289. A solution of 40 g of caustic potash and 118 g of absolute ethanol was placed in a three-necked round-bottomed flask provided with mercury-sealed stirrer, reflux condenser, thermometer, and dropping funnel. The reflux condenser was attached by rubber tubing to two cooling coils immersed in cooling mixture. The butyl 2-chloroethyl acetal (90 g) was added dropwise to the caustic potash solution over a period of two hours. The reaction mixture was then boiled under reflux for two hours. No evolution of gas occurred, and nothing was retained in the coils. The reaction mixture was then filtered under suction, and 32.7 g (i.e. 87.7% of the theoretical amount) of potassium chloride was separated. The filtrate was fractionated from a flask fitted with a Vigreux column. The residue in the flask separated into layers. The lower layer was an aqueous solution of caustic potash. The upper layer was dried with potassium carbonate and fractionated, yielding 91.5 g (96.2%) of the butyl 2-ethoxyethyl acetal, b.p. 71-72.5°/5 mm, d_4^{20} 0.8832, n_D^{20} 1.4090.

Found: MR 53.26
$C_{10}H_{22}O_3$. Calculated: MR 53.31

The substance obtained was a mobile, colorless liquid, soluble in diethyl ether, ethanol, and benzene.

Found %: C 63.22; 63.37; H 11.77; 11.80
$C_{10}H_{22}O_3$. Calculated %: C 63.12; H 11.65
Purity %: 99.9, 99.3 (iodometrically)

Synthesis of the Bis(2-ethoxyethyl)Acetal $CH_3CH(OCH_2CH_2OC_2H_5)_2$

Under the same conditions the bis(2-chloroethyl) acetal (b.p. 60.5-61.5°/1.5 mm; d_4^{25} 1.1737; n_D^{20} 1.4529) (47 g) was added with stirring over a period of four hours at 17-22° to a solution of 48 g of caustic potash in 414 g of absolute ethanol.

The mixture was heated in a boiling water bath for 15 hours. The solution became brown, and a white precipitate of potassium chloride formed. The reaction mixture was filtered under suction and was then distilled from a flask fitted with a Vigreux column. It was necessary to interrupt distillation on several occasions in order to filter off precipitated potassium chloride. The residue in the flask separated into layers, the lower layer being an aqueous solution of caustic potash. The upper layer was dried with potassium carbonate and then fractionated, yielding 10 g (19.3%) of the bis(2-ethoxyethyl) acetal, b.p. 109-110°/13 mm and 107-108°/10 mm; n_D^{20} 1.4181; d_4^{20} 0.9379.

Found MR 55.44

$C_{12}H_{22}O_4$ Calculated MR 54.95

According to Adkins [8], b.p. 83-85°/10-15 mm; and according to Nieuwland[9]: b.p. 110-114°/14 mm, d_4^{20} 0.9228, n_D^{20} 1.4163.

The substance obtained was a mobile colorless liquid, soluble in benzene.

Found: M 187.8, 189.9 (cryoscopically in benzene)

$C_{12}H_{22}O_4$ Calculated: M 206.3

Found %: C 58.13; 57.99, H 10.81; 10.93

$C_{12}H_{22}O_4$ Calculated %: C 58.22; H 10.75

Purity %: 98.3; 99.0 (iodometrically)

SUMMARY

1. A method has been developed for the synthesis of alkyl 2-ethoxyethyl acetals by the action of alcoholic solutions of alkalis on alkyl 2-chloroethyl acetals.

2. By this method the 2-ethoxyethyl ethyl and the butyl 2-ethoxyethyl acetals of acetaldehyde have been prepared and fully characterized for the first time.

3. Acetaldehyde bis(2-ethoxyethyl) acetal has been synthesized by the action of alcoholic alkali on the bis(2-chloroethyl) acetal.

4. It has been shown that under the conditions studied the 2-halogen is replaced by an alkoxyl group.

5. Under the conditions studied elimination of hydrogen halide with formation of unsaturated acetals does not occur.

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* See Consultants Bureau Translation, page 1767.
** " " " " 1367.
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IONIC COPOLYMERIZATION OF VINYL ETHERS

M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova

The polymerization of alkyl vinyl ethers is readily brought about by the action of mineral acids and metal chlorides [1]. The dissociation of "vinyl ether—catalyst" oxonium complexes depends on the temperature, occurring approximately at the boiling point of the particular ether [1].

A study of the catalytic ionic copolymerization of ethyl vinyl and butyl vinyl ethers [2] has shown that copolymerization is preceeded by polymerization of the ethyl vinyl ether, after which a copolymer formed predominantly from units of the same ether is produced. With reduction in the amount of ethyl vinyl ether monomer in the reaction mixture, 1:1 copolymers are formed, or a predominance of butyl vinyl ether units may occur. Finally the polymer of butyl vinyl ether is formed.

In order to prepare copolymers from two alkyl vinyl ethers differing in activity, it is necessary to reduce the concentration of the more active monomer to a substantial extent, or to add it continuously to the reaction mixture, in which the less active monomer is in excess.

The separation of mixtures of polymers and copolymers of various compositions is based on the dissolution and extraction of the macromolecular products with various alcohols. Thus, the polymer of ethyl vinyl ether is soluble in ethanol, and the polymer of the butyl vinyl ether in butanol. Copolymers of ethyl vinyl and butyl vinyl ethers are soluble in varying degree in isopropyl alcohol (more alcohol is required for copolymers having a predominance of butyl vinyl ether units). Such copolymers are soluble also in excess of ethanol (8–10 ml of alcohol per 1 g of copolymer). The polymer of butyl vinyl ether is soluble in butyl alcohol and is precipitated from solution by ethanol, and the polymer of ethyl vinyl ether and copolymers of ethyl vinyl and butyl vinyl ethers are precipitated from their solutions by water. By use of the method of selective dissolution and extraction of various polymerized alkyl vinyl ethers, sufficiently accurate ideas can be obtained of the course of the copolymerization of various monomers.

Ionic-copolymerization processes have been studied for the following systems, consisting of mixtures of pairs of alkyl (aryl) vinyl ethers, the alkyl (aryl) groups being: ethyl/isopropyl, ethyl/butyl, ethyl/isopentyl, ethyl/hexyl, isopropyl/butyl, butyl/heptyl, butyl/octyl, isopentyl/nonyl, isopentyl/decyl, hexyl/decyl, butyl/cyclohexyl, and butyl/phenyl.

Determinations of the refractive index of the reaction mixture were used as a check on the course of the polymerization. The course of the copolymerization process and the isolation and characterization of the products will be discussed for the example of copolymerization of ethyl vinyl and hexyl vinyl ethers.

EXPERIMENTAL

Copolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers

Expt No 1. Ethyl vinyl ether (b.p. 36°, n_D^{26} 1.3780); 72 g., i.e., 1 mole) and hexyl vinyl ether (b.p. 143.5°, n_D^{26} 1.4170); 128 g, i.e., 1 mole) were placed in a round bottomed flask fitted with reflux condenser and mechanical stirrer. The mixture was warmed to 35°, and then catalyst was added (5% solution of $FeCl_3 \cdot 6H_2O$ in butyl alcohol); the temperature then rose and the mixture thickened. The course of the copolymerization process is shown in Table 1.

The slightly yellow product, while still hot, was transferred to a Claisen flask and placed under a vacuum (15–18 mm) in a boiling water bath for two hours. The yield was 170.6 g (85%). n_D^{26} 1.4582.

a) The raw polymer was treated with three 50-ml portions of ethanol. Each extract was separately precipitated with water. Fraction I of the polymer, after being placed under vacuum (15–16 mm) in a boiling water bath for one hour had n_D^{22} 1.4486; the yield was 24 g. Fraction II had n_D^{20} 1.4490; yield 6.5 g. Fraction III had n_D^{20} 1.4503, yield 0.6 g (was not investigated further). Fractions I and II were united: total yield 30.5 g (18% on raw polymer). The isolated product was soluble in ethyl and higher alcohols, and also in ether, benzene, and acetone. It was precipitated from its solutions by water or methanol.

Found %: C 66.29, 66.23, H 11.27, 11.20

$CH_2{=}CHOC_6H_{13}$. Calculated %: C 66.59; H 11.18

ABLE 1

opolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers (1: 1)

Time	n_D^{20} of mixture	Temperature of reaction mixture (°C)	Amount of catalyst
10 hrs , 40 min	1 3975	20	–
11 " 5 "	1.3975	35	2 drops
11 " 20 "	1.4215	65	–
11 " 35 "	1 4240	60	2 drops
11 " 50 "	1 4346	85	–
12 " 5 "	1 4380	150	2 drops
12 " 20 "	1 4425	142	–
12 " 35 "	1,4425	142 5	1 drop

According to its elementary analysis the substance appeared to be a polymer of ethyl vinyl ether.

b) The undissolved material was treated with one 100-ml portion of ethanol. After vacuum treatment as before, 12.1 g (7.0%) of a product having n_D^{25} 1 4515 was obtained. The substance was soluble in the same solvents as the polymer of ethyl vinyl ether.

Found %: C 69.13; 69.06; H 11.99, 11.77.

According to its elementary analysis the product was a copolymer of ethyl vinyl and hexyl vinyl ethers corresponding to a monomer ratio of 2 : 1.

c) The ethanol-insoluble raw polymer was treated with 50 ml of a 1 : 1 mixture of hexyl and ethyl alcohols. From the extract 10·3 g (6 0% on the raw polymer) of a product having n_D^{20} 1 4528 was obtained.

Found %: C 70.37; 70 16; H 11.83; 11.99.

The analytical results indicate a copolymer having a monomer ratio of 5 : 4.

d) The raw polymer was treated twice with fresh 100-ml portions of a 1 : 1 mixture of ethyl and hexyl alcohols. The products isolated were found to be close with respect to refractive index (1 4557 and 1.4560), and they were united. The yield was 73.2 g (43%). n_D^{25} 1.4558.

Found %: C 71.73, 71.59; H 12.14, 12.18

$CH_2{=}CHOC_2H_5 + CH_2{=}CHOC_6H_{13}$ Calculated %: C 72; H 12

e) The residual raw polymer (2 g, n_D^{25} 1.4600), which was insoluble in the mixture of ethyl and hexyl alcohols, dissolved completely in hexyl alcohol. It was not investigated further.

The total yield of polymers and copolymers was 128.7 g (75.4% on the raw polymer).

Expt No. 2. Ethyl vinyl ether (36 g, i.e., 0.5 mole) and hexyl vinyl ether (128 g, i.e., 1 mole) were placed in the flask (the apparatus and the constants of the ethers were the same as in Expt. No. 1). The course of the copolymerization is shown in Table 2

TABLE 2

Copolymerization of Ethyl Vinyl and Hexyl Vinyl Ethers (1:2)

Time	n_D^{20} of mixture	Temperature of reaction mixture (°C)	Amount of catalyst (drops)
10 hrs. 10 min.	1 4040	21	–
10 " 30 "	1 4040	35	2
10 " 45 "	1.4270	72	–
11 " 0 "	1.4285	67	2
11 " 15 "	1.4377	123	–
11 " 30 "	1.4400	124	2
11 " 45 "	1.4486	148	–
12 " 0 "	1.4490	144	1
12 " 15 "	1 4492	145	–

After vacuum treatment under the conditions of Expt. No. 1, 141.6 g (86.8%) of substance n_D^{25} 1.4605, was obtained.

a) The raw polymer was treated with 100 ml of ethanol. The polymer that dissolved in the ethanol was precipitated with water. Solvent was driven off, and the product was placed under vacuum in a boiling water bath for about one hour. The yield was 10 0 g (7% on the raw polymer); n_D^{20} 1.4518.

Found %: C 69.58; 69.35; H 12.00; 11.82

The copolymer, according to its elementary analysis, refractive index, and solubility, corresponded to that described in Expt. No. 1 b

b) The ethanol-insoluble raw polymer was treated with 50 ml of a mixture of ethyl and hexyl alcohols (1 : 1) From the extract 17.2 g (12%) of a product of n_D^{20} 1.4525 was obtained.

Found %: C 70.64; 70.52; H 11.78; 12 02.

This copolymer, according to its elementary analysis, was close to that described in Expt. No 1c

c) The raw polymer was treated with two 150-ml portions of a 1 : 1 mixture of ethyl and hexyl alcohols. From the extract 37.6 g (27%) of a product of n_D^{20} 1.4563 was obtained. It corresponded in its properties to the copolymer described in Expt. No. 1d.

d) The raw polymer was treated with 75 ml of the same solvent (c). From the extract 2.8 g (2%) of a product of n_D^{20} 1.4568 was obtained.

Found %: C 71.13, 71.05; H 11.79; 11.92.

TABLE 3

Characteristics of Copolymers of Vinyl Ethers

Composition of Copolymer	Yield (%)	d_4^{20}	n_D^{20}	Absolute viscosity of a 0.1 M benzene solution at 20° (centipoise)	Molecular weight found	Degree of polymerization	Found % C	Found % H	Solubility
$[CH_2=CHOC_2H_5 + CH_2=CHOCH(CH_3)_2]_n$	52	0.9270	1.4510	0.7307	4295	54	68.15	11.27	Soluble in ethyl and higher alcohols, ether, benzene, acetone
$[CH_2=CHOC_2H_5 + CH_2=CHOC_4H_9]_n$	54	0.9245	1.4530	0.7349	2150	25	70.16	11.99	"
$[CH_2=CHOC_2H_5 + CH_2=CHOCH_2CH_2CH(CH_3)_2]_n$	48	0.9244	1.4542	0.6885	1691	18	69.86	11.45	"
$[CH_2=CHOC_2H_5 + CH_2=CHOC_6H_{13}]_n$	43	0.9233	1.4558	0.8054	3919	39	71.73	12.14	"
$[CH_2=CHOCH(CH_3)_2 + CH_2=CHOC_4H_9]_n$	75	0.9230	1.4545	0.7330	2084	22	70.71	11.21	Soluble in propyl and higher alcohols, ether, benzene, acetone
$[CH_2=CHOC_4H_9 + CH_2=CHOC_7H_{15}]_n$	79	0.9260	1.4590	0.8662	4612	38	73.98	12.44	Soluble in butyl and higher alcohols, ether, benzene, acetone
$[CH_2=CHOC_4H_9 + CH_2=CHOC_8H_{17}]_n$	76	0.9243	1.4620	0.9595	7034	55	74.14	12.56	"
$[CH_2=CHOCH_2CH_2CH(CH_3)_2 + CH_2=CHOC_8H_{15}]_n$	50	0.9198	1.4623	0.8311	3262	23	75.59	12.65	Soluble in isopentyl and higher alcohols, ether, benzene, acetone
$[CH_2=CHOCH_2CH_2CH_2CH(CH_3)_2 + CH_2=CHOC_{10}H_{21}]_n$	51	0.9217	1.4670	0.6464	3482	23	75.86	12.75	"
$[CH_2=CHOC_6H_{13} + CH_2=CHOC_{14}H_{29}]_n$	59	0.9231	1.4657	0.8807	4710	30	76.38	12.90	Soluble in hexyl and higher alcohols, ether, benzene
$[CH_2=CHOC_4H_9 + CH_2=CHOC_8H_{11}]_n$	62	0.9316	1.4800	0.8618	4125	36	74.23	11.59	Soluble in butyl alcohol, ether, benzene
$[CH=CHOC_4H_9 + CH_2=CHOC_6H_5]_n$	49	0.9620	1.5070	0.7312	1661	15	75.99	9.17	

The analytical results indicate a copolymer having a monomer ratio of 4 : 5.

e) Raw polymer insoluble in the alcohol mixture was completely soluble in 150 ml of hexyl alcohol, and was precipitated from solution by 200 ml of ethanol. After removal of solvents by distillation and vacuum treatment to constant weight, the yield of product was 46.3 g (33%); n_D^{20} 1.4633. According to its properties the product was a polymer of hexyl vinyl ether.

Found %: C 74.79; 74.89; H 12.59; 12.38

$[-C_6H_{13}OCH=CH_2-]_n$ Calculated %: C 74.94; H 12.59

The total yield of polymers and copolymers was 113.9 g (81% on the raw polymer).

The properties of copolymers in which the original monomers occur in the ratio of 1 : 1 are given in Table 3.

In order to verify the accuracy of the method of selective separation of polymers, polymerized ethyl vinyl ether (n_D^{20} 1.4518) and polymerized hexyl vinyl ether (n_D^{20} 1.4630) (50 g of each) were taken and mixed carefully. The homogeneous mixture was first treated with three 80-ml portions of ethanol, polymer being then precipitated with water. From the first extract 24 g of polymerized ethyl vinyl ether was obtained, from the second 16.5 g, and from the third 2 g. The total yield of polymerized ethyl vinyl ether was 42 g (84%); n_D^{20} 1.4515—1.4520. The ethanol-insoluble polymer dissolved completely in 140 ml of hexyl alcohol and was reprecipitated with 250 ml of ethanol. The yield of polymerized hexyl vinyl ether was 46 g (92%); n_D^{20} 1.4635.

SUMMARY

1. A study has been made of the copolymerization of alkyl (C_4—C_{12}) vinyl ethers.

2. The copolymers obtained have been characterized by elementary analysis, solubility, viscosity, and molecular weight determinations.

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Institute of Organic Chemistry
of the USSR Academy of Sciences

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[1] M. F. Shostakovsky, Monograph "Vinyl ethers," Acad. Sci. USSR Press, Moscow, 1952.

[2] M. F. Shostakovsky, B. I. Mikhantyev, and V. A. Serebrennikova, Chemistry and Physical Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press, Moscow, 1952, p. 35.

NOMENCLATURE OF SYNTHETIC STEROIDS AND RELATED SUBSTANCES*

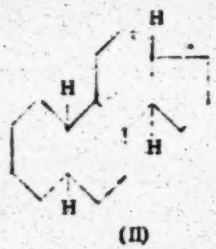
I. N. Nazarov

During the last seven years extensive and systematic investigations have been proceeding in our laboratory on the synthesis of steroid compounds and related substances. These investigations have led to the synthesis of numerous polycyclic compounds derived from hydrogenated cyclopentaphenanthrene, chrysene, benzofluorene, and their heterocyclic (sulfur) analogs. With the appearance of these compounds an urgent need arose for the development of a general system of nomenclature that would cover not only the synthetic steroids known at present, but would be suitable for the description of any new steroid compounds and related substances, which will no doubt appear in the future in ever increasing number.

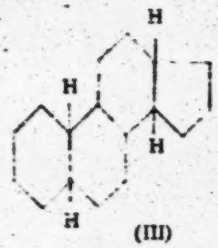
The nomenclature recently adopted at a London conference [1] for steroids is applicable only to natural products and is intended for the description of steroids of any one strictly defined spatial configuration. This nomenclature does not permit the description of synthetic steroid compounds that are distinct from the natural steroids and must often be dealt with in the performance of a complete synthesis.

For the description of synthetic steroid compounds, irrespective of their optical activity or membership of a particular series of natural steroids and taking into account only the spatial structure of the steroid skeleton, we propose the following eight names for the fundamental hydrocarbons of the perhydrocyclopenta[a]phenanthrene series and the perhydrochrysene series:

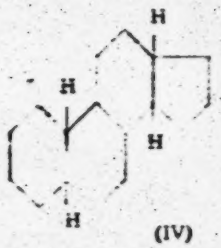
(I)
Allosterane



(II)
Sterane

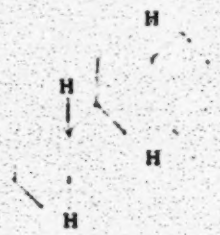


(III)
Allocardosterane
(Allisosterane)

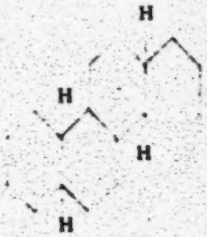


(IV)
Cardosterane
(isosterane)

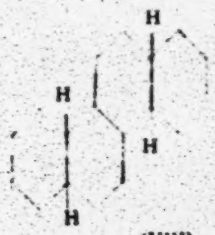
(V)
Allochrysane
D-Homoallosterane)



(VI)
Chrysane
(D-Homosterane)



(VII)
Allocardochrysane
(D-Homoallocardo-
sterane)



(VIII)
Cardochrysane
(D-Homocardo-
sterane)

* In view of the nature of this article, the names of compounds have been transcribed as directly as possible. American practice, however, has been followed for indicating positions of double bonds ($\Delta^{9,11}$, etc. is used in the original). The Russian ending –an has been transcribed as –ane for fully saturated compounds, and in other cases as –an. (Publisher.)

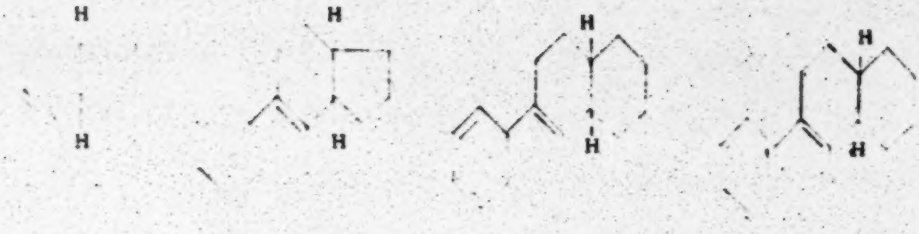
The fundamental steroid hydrocarbons containing one aromatic ring A or two aromatic rings A and B, which form the basis for the estrogenic hormones of the estrone and equilenin groups, receive the following names:

(IX) Estrosteran

(X) Isoestrosteran

(XI) Estrochrysan (D-Homoestrosteran)

(XII) Isoestrochrysan (D-Homoisoestrosteran)



(XIII) Equisteran

(XIV) Isoequisteran

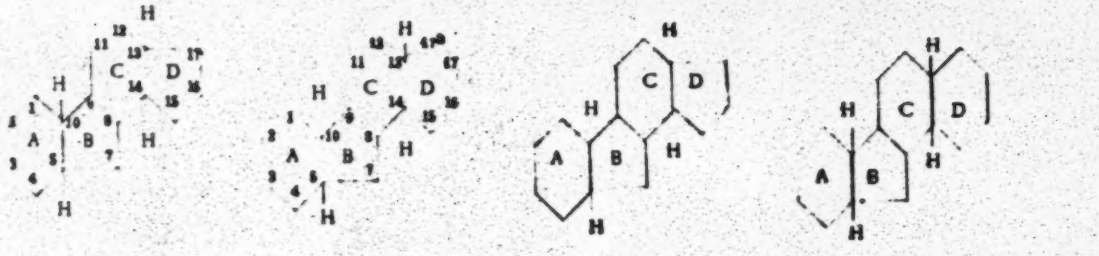
(XV) Equichrysan (D-Homoequisteran)

(XVI) Isoequichrysan (D-Homoisoequisteran)

Ring Enlargement and Contraction

When ring enlargement occurs, the extra atom of the homosteroid compound preserves the number of the preceding carbon atom with addition of the letter "a" (see Formulas V and XVIII).

When ring contraction occurs, a carbon atom is removed, and all the remaining atoms in the norsteroid compound retain their usual numbers (see Formulas XVII and XVIII):



(XVII) B-Norsterane

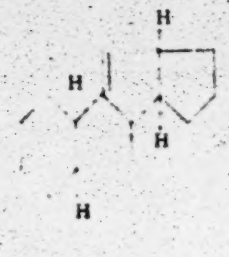
(XVIII) B-Norchrysane

(XIX) B-Norcardisterane

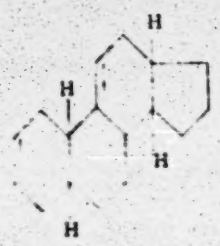
(XX) B-Norcardochrysane

Indication of Double Bonds

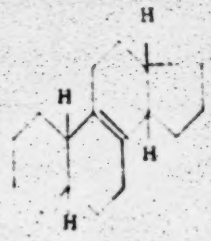
Double bonds are indicated in the usual way, except in the case of the chrysane hydrocarbons, the introduction of one double bond into which is indicated by the addition of the suffix -ene to the name of the hydrocarbon itself (see Formulas XXIV and XXVI):



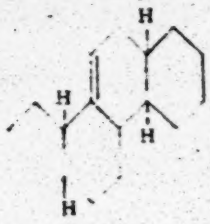
(XXI)
9(11)-Sterene



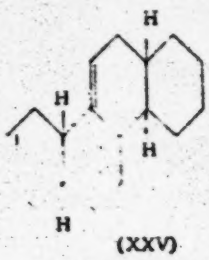
(XXII)
2,9(11)-Steradiene



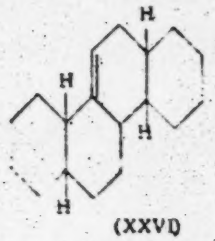
(XXIII)
8(9)-Cardosterene



(XXIV)
9(11)-Chrysanene



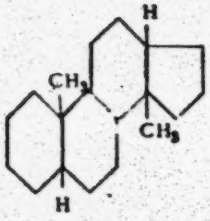
(XXV)
2,9(11)-Chrysadiene



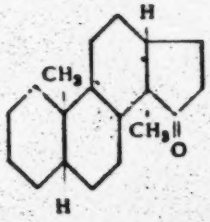
(XXVI)
9(11)-Cardochrysanene

Indication of Substituents and Functional Groups

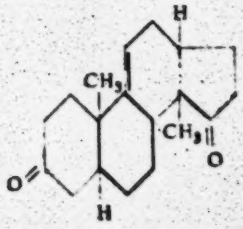
The orientation of substituents is indicated in the accepted way, the position of the substituent being given and its spatial orientation being indicated by means of the letters α and β (α for trans and β for cis. configuration)



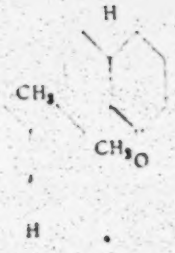
(XXVII)
10,14-Dimethylcardosterane



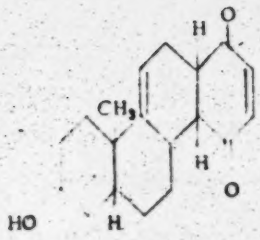
(XXVIII)
10,14-Dimethyl-8-cardosteren-15-one



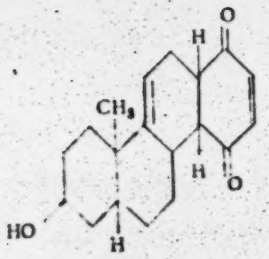
(XXIX)
10,14-Dimethyl-9-cardosterene-3,15-dione



(XXX)
10,14-Dimethyl-2,9-cardochrysadien-15-one



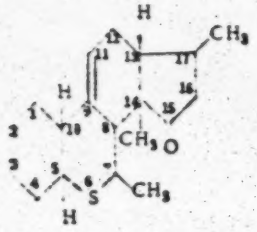
(XXXI)
10-Methyl-9,16-cardochrysadien-3α-ol-15,17a-dione



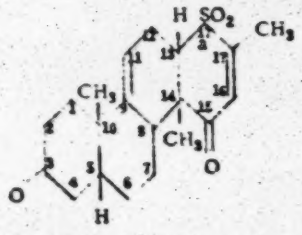
(XXXII)
10-Methyl-9,16-cardochrysadien-3β-ol-15,17a-dione

Indication of Hetero Atoms

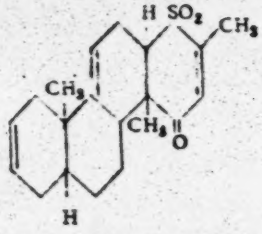
In the process of complete synthesis compounds may be prepared containing hetero atoms (oxygen, sulfur, or nitrogen) in the steroid nucleus, the following terms are used to indicate these: O – oxa; S – thia; SO_2 – sulfa, NH – aza. The hetero atoms are included in the numbering of the steroid skeleton.



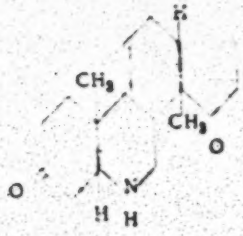
(XXXIII)
7,14,17 Trimethyl-6-thia-9(11)-cardosteren-15-one



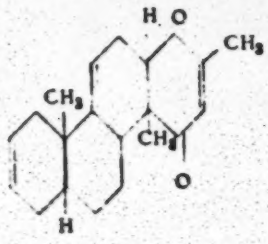
(XXXIV)
10,14,17-Trimethyl-17a-sulfa-9,16-cardochrysadiene-3,15-dione



(XXXV)
10,14,17-Trimethyl-17a-sulfa-2,9,16-cardochrysatrien-15-one



(XXXVI)
10,14-Dimethyl-6-aza-9-cardosterene-3,15-dione



(XXXVII)
10,14,17-Trimethyl-17a-oxa-2,9,16-cardochrysatrien-15-one

We shall use the nomenclature described above in all cases in which the steroid compounds obtained cannot be identified with any natural products.

SUMMARY

A system of nomenclature has been proposed for synthetic steroid compounds.

LITERATURE CITED

[1] Helv. Chim. Acta 34, 1680 (1951).

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Institute of Organic Chemistry,
USSR Academy of Sciences

ACETYLENE DERIVATIVES

COMMUNICATION 151. HETEROCYCLIC COMPOUNDS

XXVII. SYNTHESIS OF POLYCYCLIC γ-AMINO ALCOHOLS AND THEIR ESTERS*

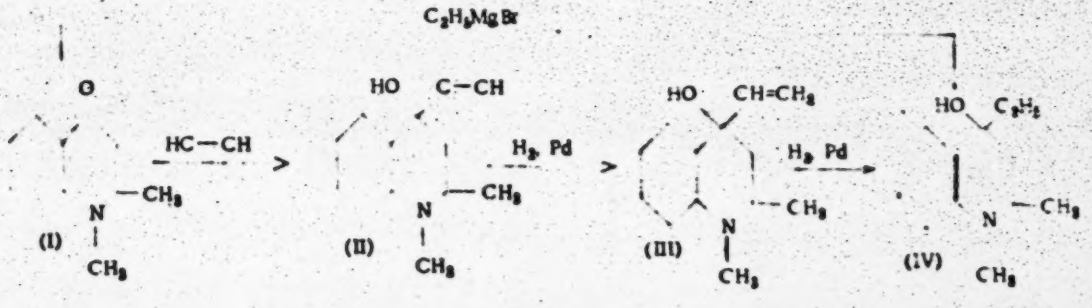
I. N. Nazarov, L. I. Ukhova, and V. A. Rudenko

In the preceding paper [1] we described the synthesis of a number of bicyclic and tricyclic compounds taining a condensed 4-piperidone ring. In view of the fact that certain esters of 4-piperidinols are of high physiological activity, we decided to synthesize a number of bicyclic and tricyclic γ-amino alcohols and their esters.

When octahydro-1,2-dimethyl-4(1H)-quinolone (I) was condensed with acetylene in dry ethereal solution in presence of caustic potash in powder form, 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) was obtained in about 40% yield. Numerous attempts to increase the yield by changing the temperature and duration of the reaction did not lead to improved results; an appreciable amount of unchanged ketone (I) was always recovered after the reaction. This ketone condensed with acetylene also in the presence of the potassium derivative of 2-methyl-2 hexanol, but in this case also a considerable proportion of the original ketone (I) was recovered unchanged, and the yield of the acetylenic alcohol (II) was again not more than 40%. The difficulty with which these reactions went was unexpected since we have previously shown in our laboratory [2] that the condensations of various 4-piperidones (including octahydro-2-methyl-4(1H)-quinolone) with acetylene in presence of caustic potash proceed smoothly and give high yields of the corresponding acetylenic alcohols. Finally, we condensed octahydro-1,2-dimethyl-4(1H)-quinolone (I) with sodium acetylide in liquid ammonia [3], and so obtained 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in 82% yield.

It should be noted that the main product of the condensation of acetylene with the ketone (I) was in all cases the crystalline acetylenic alcohol (II), m.p. 130-131°, which on partial hydrogenation (one molecule of hydrogen) in presence of a Pd catalyst gave decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III), m.p. 94-95°, and on exhaustive hydrogenation (two molecules of hydrogen) gave 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°.

In the exhaustive hydrogenation of the acetylenic alcohol (II), prepared in liquid ammonia, a very small amount of a second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) of m.p. 106-106.5° was obtained, and this was the sole product obtained from the reaction of ethylmagnesium bromide on octahydro-1,2-dimethyl-4(1H)-quinolone (I). Thus, exhaustive hydrogenation of the acetylenic alcohol (II) yields the high isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) (m.p. 147-148°), whereas the action of ethylmagnesium bromide on the ketone (I) yields the low melting isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV) (m.p. 106-106.5°). A similar phenomenon – a difference in steric directivity in acetylenic and Grignard syntheses – has been observed previously in other cases by Nazarov and Raigorodskaya [2].



Condensation of octahydro-1,2-dimethyl-4(1H)-quinolone (I) with 1-buten-3-yne in presence of caustic potash powder yielded 4-(3-buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V) in 80% yield, and this, on being fully hydrogenated in presence of Pd and Pt catalysts, yielded 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI), m.p. 119-120°.

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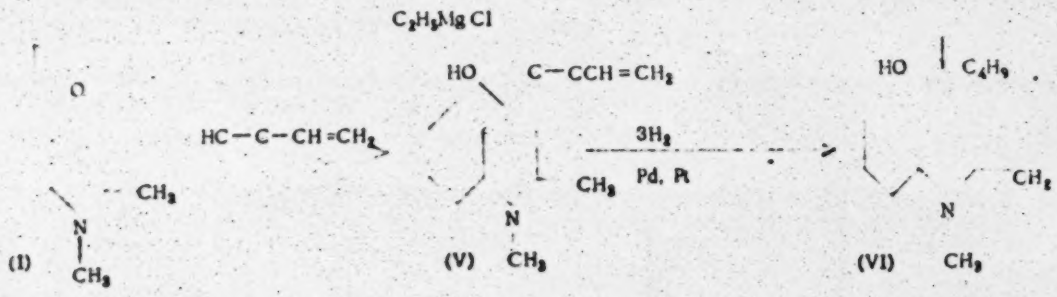
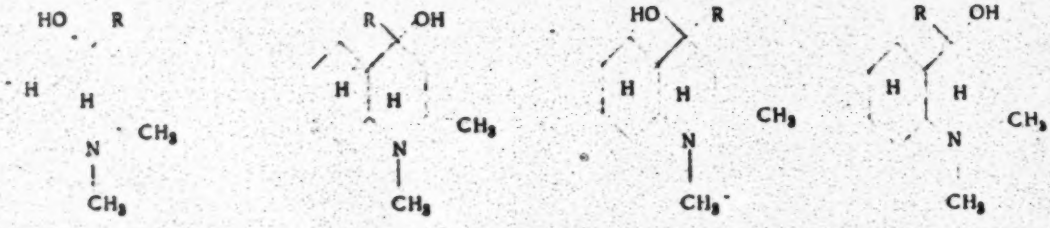
By reaction of octahydro-1,2-dimethyl-4(1H)-quinolone (I) with butylmagnesium chloride, a second isomer of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI) of m.p. 38-99° was obtained. In this case also, therefore, the condensations of 1-buten-3-yne and of butylmagnesium chloride with the ketone (I) differ in steric selectivity:



We synthesized also certain tertiary alcohols by the action of phenyllithium on bicyclic and tricyclic compounds containing a condensed 4-piperidone ring.

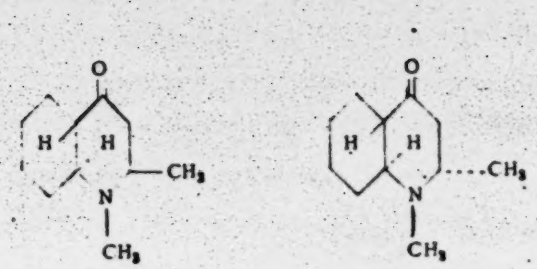
Reaction of phenyllithium with octahydro-1,2-dimethyl-4(1H)-quinolone (I) gave a 70% yield of a mixture of two crystalline isomers of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII), from which a low melting isomer, m.p. 113-114°, and a high melting isomer, m.p. 167.5-168°, were isolated:

All the above described isomeric alcohols (II ÷ VII) must belong to the trans-decahydroquinoline series, and the difference in their properties must depend solely on the spatial arrangement of the substituents R and OH at $C_{(4)}$ of the decahydroquinoline nucleus:

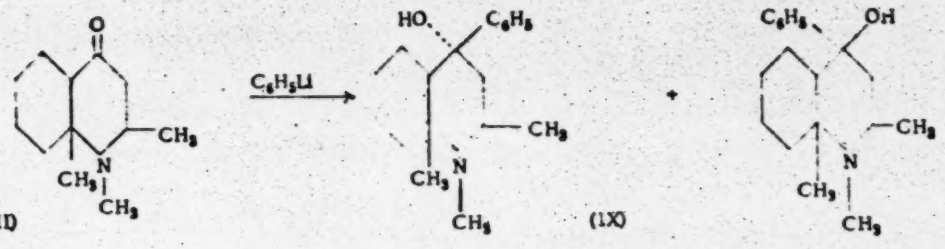


R = CH≡C, CH_2=CH, C_2H_5, CH_2=CH—C≡C, C_4H_9, C_6H_5.

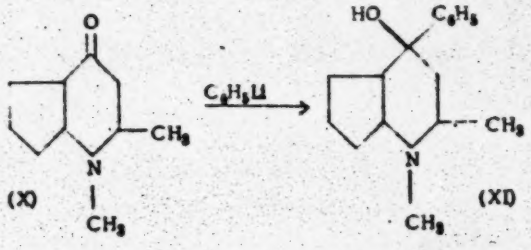
It is probable that the spatial configuration of the methyl at $C_{(2)}$ remains constant in these alcohols, for they are obtained from pure trans-octahydro-1,2-dimethyl-4(1H)-quinolone (I), the spatial configuration of which may be represented by one of the following formulas:



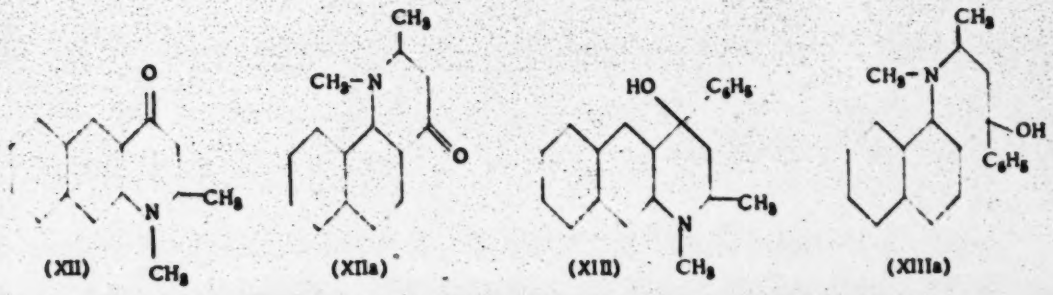
Reaction of phenyllithium with octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII) yielded decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in 62% yield, and this also was isolated in two stereoisomeric forms, m.p 130-132° and 164-165°:



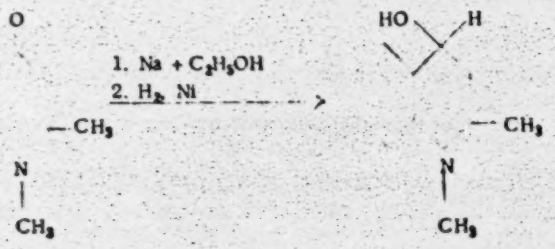
When phenyllithium was condensed with hexahydro-1,2-dimethyl-1,5H-pyrindin-4(1H)-one (X), octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI) was obtained in 66% yield. It was a viscous liquid, and it was not found possible to bring about crystallization:



Reaction of phenyllithium with dodecahydro-1,2-dimethylbenzo[g or h]quinolin-4(1H)-one (XII or XIIa) yielded tetradecahydro-1,2-dimethyl-4-phenylbenzo[g or h]quinolin-4-ol (XIII or XIIIa):



When octahydro-1,2-dimethyl-4(1H)-quinolone was reduced with sodium in alcohol, or by catalytic hydrogenation, a mixture of stereoisomers of decahydro-1,2-dimethyl-4-quinolinol (XIV) was obtained:



A number of ketones and esters of the piperidine series with strong sedative properties have been recently described in the literature. They include ethyl 1-methyl-4-phenylisonipecotate (Lydol, Dolantin, Demerol) [4], the propionic esters of 1-methyl-4-phenyl-4-piperidinol [5] and 1,3-dimethyl-4-phenyl-4-piperidinol [6], 4-(m-hydroxyphenyl)-1-methyl-4-propionylpiperidine (Cliradon) [7], and others. Among numerous esters of 4-piperidinols synthesized in our laboratory in recent years [8], some were found to have very powerful sedative (analgetic or anesthetic) properties. However, no esters of polycyclic compounds having a condensed piperidine ring have yet been described.

We considered it to be of interest to synthesize compounds of this type in order to determine their physiological activity.

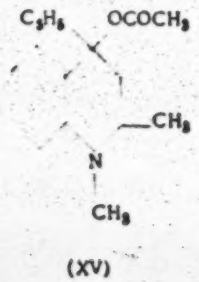
In carrying out this task we met a number of difficulties. Thus it was found that when the lithium derivative of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) was treated with acid chlorides, the original alcohol was recovered unchanged, being incapable of esterification under these conditions. Spassow's method [9], which readily yields esters when amino alcohols are treated with acid chlorides in presence of magnesium, was also found to be inapplicable to the synthesis of tertiary α-phenyl alcohols of the decahydroquinoline series.

When the alcohol (VII) was treated with acetic or propionic anhydride in presence of sulfuric acid, the original alcohol was again recovered unchanged, no esterification occurring. Esters of both of the isomers of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) were obtained by the action of acid anhydrides in pyridine at 140°. However, only the acetates (XV) and propionates (XVI) could be obtained in this way, and all attempts to prepare the benzoates by the action of benzoyl chloride in pyridine (or in absence of pyridine) did not give positive results, unchanged alchol (VII) being recovered in all experiments.

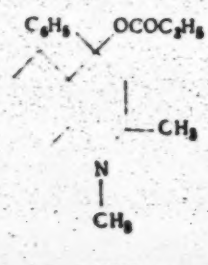
When acetic anhydride was heated with either of the isomers of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in pyridine at 140-180° or in presence of sulfuric acid at 100-120°, the original tertiary alcohol (IX) was recovered unchanged, as was shown by mixed melting-point tests on the hydrochlorides.

This difference in the behaviors of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) and decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) toward esterifying agents is evidently to be explained by the presence in the latter of an angular methyl group in the 8a-position, which results in steric hindrance to the esterification of the hydroxyl in the 4-position.

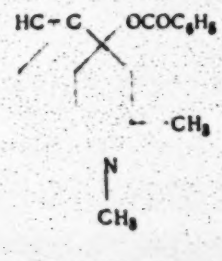
Reaction of benzoyl chloride with 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in pyridine at 100° yielded its benzoic ester (XVII), and reaction of benzoyl chloride with decahydro-1,2-dimethyl-4-quinolinol (XIV) yielded its benzoic ester (XVIII):



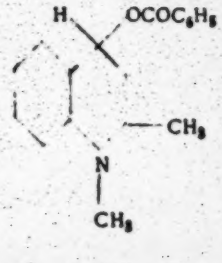
(XV)



(XVI)



(XVII)



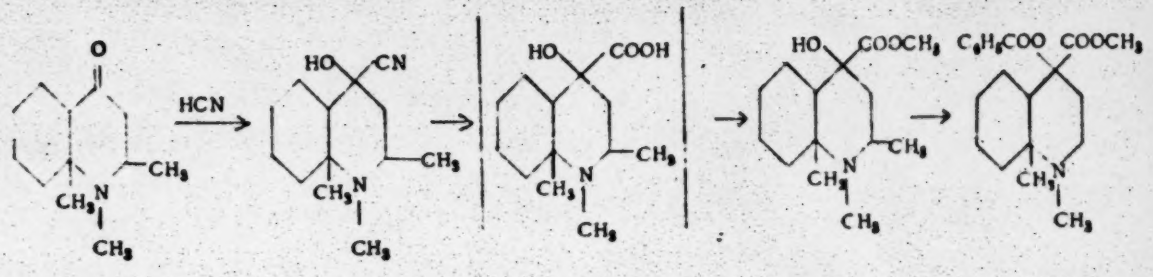
(XVIII)

The benzoic esters (XVII and XVIII) did not give stable crystalline salts, and were therefore not tested.

Physiological tests on the acetate (XV) and the propionate (XVI) (high melting isomers) showed that both of these compounds had anesthetic action, which was more marked in the propionic ester. The activities of these compounds, however, were lower than those of preparations now in use in medical practice, and their toxicities were higher.

The cyanohydrin (XIX) was obtained from octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII), and this, on being hydrolyzed, gave the corresponding hydroxy acid (XX), which was obtained in the form of its hydrochloride

Esterification of this acid with methanol, with passage of hydrogen chloride, yielded methyl decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI), m.p. 138-139°, and by the action of benzoyl chloride on this hydroxy ester, methyl 4-benzoyloxydecahydro-1,2,8a-trimethylcinchoninate (XXII), m.p. 256-257°, was obtained:



(VIII) (XIX) (XX) (XXI) (XXII)

The benzoic ester (XXII) is close in structure to *a*-eucaine; physiological tests on this substance will therefore be of interest.

EXPERIMENTAL

4-Ethynyldecahydro-1,2-dimethyl-4-quinolinol (II)

a) Liquid ammonia (300 ml) was placed in a three-necked, round-bottomed flask fitted with mechanical stirrer, reflux condenser, dropping funnel, thermometer, and tube for passage of acetylene. The flask was cooled with a mixture of dry ice and methanol (−70°), and sodium (9 g) was added in small pieces. When the whole of the sodium had dissolved, passage of acetylene was begun and about 60 liters passed into the flask in the course of three hours. Then, with continuous stirring and passage of acetylene, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (30 g), b.p. 100-102°/2 mm, n_D^{19} 1.4980 [10], in an equal volume of dry ether was added dropwise over a period of 20 minutes. After addition of the ketone, acetylene was passed for a further 90 minutes, and the reaction mixture was set aside overnight. On the next day ammonium chloride (30 g) and water (50 ml) were added to the reaction mixture at −15°. The mixture was repeatedly extracted with ether, and the ethereal solution was neutralized with carbon dioxide until it became clear; it was then dried with magnesium sulfate and vacuum-fractionated, yielding 28.3 g (82%) of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) as a colorless, very viscous (glasslike) liquid, b.p. 129-131°/3 mm.

	Found %:	C 75.09; 74.93;	H 10.51; 10.50
$C_{13}H_{21}ON$.	Calculated %:	C 75.29;	H 10.21

This substance is of good solubility in alcohol, benzene, chloroform, carbon tetrachloride, dioxane, acetone, and various gasoline fractions.

b) A mixture of 18.6 g of caustic potash in powder form and 200 ml of dry ether was saturated with acetylene, which was passed for one hour at −3°. A solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (30 g) in dry ether (30 ml) was then added dropwise for a period of one hour with continuous stirring and passage of acetylene, which was then passed for a further period of 4 hr, 30 min., the temperature being maintained at −3° throughout. On the next

...the reaction mixture was treated with 30 ml of water, and the product was carefully extracted with ether; ...e ether extract was neutralized with carbon dioxide until it became clear, and was then dried with magnesium ...ulfate and vacuum-fractionated, yielding 27.3 g of a colorless viscous liquid, b.p. 134-137°/4 mm, which, on ...being diluted with gasoline (b.p. 80-100°), partially crystallized out. Two recrystallizations from gasoline yielded 4 g of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol (II) in the form of colorless crystals, m.p. 130-131°.

	Found %:	N 6.77, 6.79
$C_{13}H_{21}ON$	Calculated %:	N 6.75

The picrate, recrystallized from alcohol, melted at 188-189°.

The noncrystallizing mother liquor, after separation of the crystals of the acetylenic alcohol (II), was vacuum-distilled yielding a fraction (I, 8g), b.p. 130-137°/5 mm, which appeared to be a mixture of the original ketone (I) and the acetylenic alcohol (II), and a fraction (II, 9 g), b.p. 137-139° 5mm), which appeared to be the pure acetylenic alcohol (II). The total yield of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol was 13 g [about 40% on the amount of the ketone (I) taken]

c) Potassium (19.5 g) was dissolved in 232 g of 2-methyl-2-hexanol (b.p. 140-141°), and the excess of the alcohol was distilled off under reduced pressure. The dry alkoxide that remained behind was mixed with absolute ether, giving a slurry (150 ml), which was then saturated with acetylene for two hours at −10°. On the next day the product was treated with water (30 ml) and extracted with ether; the ether extract was neutralized with carbon dioxide until it became clear, and was dried with magnesium sulfate and vacuum-fractionated, yielding:

Fraction I, b.p. 103−125°/2.5 mm	5.1 g
Fraction II, b.p. 125−128°/2.5 mm	21.5 g
Resinous residue	3.0 g

Fraction II, after addition of gasoline and three crystallizations, yielded 6 g of the crystalline acetylenic alcohol (II), m.p. 130-131°. The noncrystallizing mother liquor was vacuum-distilled, yielding 3 g of a mixture of the original ketone (I) and the acetylenic alcohol (II), b.p. 120-130°/3 mm, and 8 g of a viscous liquid, b.p. 130-132° 3 mm, which solidifed to a glasslike mass and appeared to be pure acetylenic alcohol (II). The total yield of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol was 14 g [about 41% on the amount of ketone (I) taken]

Decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III)

The crystalline acetylenic alcohol (II) (3 g, m.p. 130-131°) was dissolved in ethanol (20 ml) and hydrogenated in the presence of a Pd catalyst. When 351 ml (19°, 748.6 mm) of hydrogen had been absorbed, the process was discontinued. The alcohol was distilled off, and the residue was vacuum-distilled, yielding 2.5 g of decahydro-1,2-dimethyl-4-vinyl-4-quinolinol (III), b.p. 132-134°/5 mm, which rapidly crystallized out. After three crystallizations from petroleum ether it melted at 93.5-95°.

	Found %:	C 74.77, 74.71; H 11.00; 10.99
$C_{13}H_{23}ON$	Calculated %:	C 74.92; H 11.07

4-Ethyldecahydro-1,2-dimethyl-4-quinolinol (IV)

a) The crystalline alcohol (II) (m.p. 130-131°, 0.9 g) was dissolved in ethanol (10 ml) and hydrogenated in presence of a Pd catalyst. When 200 ml (19°, 744.7 mm) of hydrogen had been absorbed, the process was discontinued (theoretically, 217 ml of hydrogen is required for the complete hydrogenation of the triple bond). The catalyst was filtered off, the alcohol was distilled off, and the crystals that came down were recrystallized twice from gasoline, yielding 0.7 g of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°.

	Found %:	C 73.73; 73.93, H 12.01; 11.83
$C_{13}H_{25}ON$	Calculated %:	C 73.87 H 11.92

A similar result was obtained also when the above described (b) liquid fraction of the acetylenic alcohol (II), b.p. 137-139°/5 mm, was exhaustively hydrogenated. The isomer of the saturated alconol (IV) obtained by this method did not give a picrate.

b) Magnesium turnings (4.5 g) and absolute ether (100 ml) were introduced into a three-necked, round-bottomed flask, and ethyl bromide (20 g) was added dropwise. To the ethylmagnesium bromide so obtained, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (16.5 g) in an equal volume of absolute ether was added dropwise, with stirring and cooling with ice water. The reaction mixture was stirred for one hour at room temperature and then set aside overnight. On the next day it was boiled for two hours. After removal of ether and addition of 70 ml of absolute toluene, the mixture was stirred for a further 2 hr, 30 min at the temperature of boiling

toluene. The reaction mixture was then treated with 15% hydrochloric acid (25 ml) and the toluene layer was separated and extracted with 15% hydrochloric acid (20 ml). The united aqueous layer was saturated with solid caustic alkali, and the base that separated was extracted with ether. The ether layer was dried with magnesium sulfate and vacuum-fractionated, yielding 9 g of the original ketone (I), b.p. 108-110°/5 mm; n_D^{20} 1.4950) and 3.4 g of a colorless liquid, b.p. 129-131°/5 mm, which crystallized out in the receiver. After two recrystallizations from gasoline, 2.9 g of the second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 106-106.5°, was obtained.

	Found %:	C 74.00; 74.10;	H 12.14; 11.91
$C_{13}H_{25}ON$.	Calculated %:	C 73.87	H 11.92

	Found %:	OH 7.71 (by Chugaev-Tserevitinov method)
$C_{13}H_{24}(OH)N$.	Calculated %:	OH 8.04

The picrate, after recrystallization from alcohol, melted at 164.5-166°.

c) The acetylenic alcohol formed by the condensation reaction in liquid ammonia (II), b.p. 129-131°/3 mm, (see a) in the section relating to this substance) (6 g) was dissolved in ethanol (60 ml) and hydrogenated in the presence of a Pd catalyst, 1420 ml (20°, 745 mm) of hydrogen being absorbed. The catalyst was filtered off, the alcohol was distilled off, and the product was vacuum-distilled, yielding 4.7 g of a colorless liquid, b.p. 115-116°/2 mm, which crystallized out in the receiver. After recrystallization from gasoline, the product melted at 90-140°. Fractional crystallization yielded 3.9 g of the above described isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol (IV), m.p. 147-148°. From the mother liquor, after long standing, a few crystals of the second isomer of 4-ethyldecahydro-1,2-dimethyl-4-quinolinol appeared, and these, after being washed with gasoline and dried in a vacuum desiccator, melted at 104-105°. In admixture with the above described sample obtained by the Grignard method, it showed no depression in melting point.

4-(3-Buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V)

Caustic potash in powder form (14 g) and dry ether (50 ml) were introduced into a round-bottomed flask, and in small portions, with continuous stirring and cooling to −10°, 1-buten-3-yne (30 g) and octahydro-1,2-dimethyl-4(1H)-quinolone (I) (25 g) dissolved in dry ether (30 ml) were added. The reaction mixture was cooled with ice water and stirred for 6 hrs. 30 min.; on the next day it was treated with water (20 ml). The product was extracted with ether, and the ether extract was neutralized with carbon dioxide until clear, dried with magnesium sulfate, and vacuum distilled in a current of nitrogen, yielding 25 g of 4-(3-buten-1-ynyl)decahydro-1,2-dimethyl-4-quinolinol (V) in the form of a clear colorless liquid, b.p. 138-140°/2mm, which solidified after the distillation to a glasslike mass.

	Found %:	N 5.79; 5.73	
$C_{15}H_{25}ON$.	Calculated %:	N 6.00	

4-Butyldecahydro-1,2-dimethyl-4-quinolinol (VI)

a) The freshly distilled α-butenynyl alcohol (V) (b.p. 138-140°/2 mm; 3.3 g) was dissolved in ethanol (20 ml) and hydrogenated in presence of a Pd catalyst, the process being discontinued when 700 ml of hydrogen had been absorbed. A portion of Pt catalyst was added, and a further 325 ml of hydrogen was absorbed. The theoretically required amount of hydrogen was 1054 ml (16°, 746 mm). The catalyst was filtered off, the alcohol was distilled off, and the product was vacuum-distilled, yielding 2.6 g of a colorless, not particularly viscous liquid, b.p. 115-117°/2.5 mm, which partially crystallized out in a short time. Two crystallizations from gasoline yielded 1.05 g of crystals of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI), m.p. 119-120°, readily soluble in alcohol, benzene, chloroform, carbon tetrachloride and acetone.

	Found %:	C 75.61; 75.42;	H 12.32; 12.22
$C_{15}H_{29}ON$.	Calculated %:	C 75.25;	H 12.21

b) Magnesium turnings (4 g), absolute ether (50 ml), and butyl chloride (15.3 g) were introduced into a round-bottomed flask, and to the Grignard reagent so prepared, a solution of octahydro-1,2-dimethyl-4(1H)-quinolone (I) (15 g) in absolute ether (15 ml) was added with stirring and cooling (ice water). Stirring was continued for five hours with cooling and for five hours at the boiling point of ether. The reaction mixture was cooled, and 15% hydrochloric acid (120 ml) was added. The ether layer was separated and extracted with dilute hydrochloric acid, and the united aqueous layer was saturated with solid caustic alkali. The product was carefully extracted with ether, and the extract was neutralized with carbon dioxide, dried with magnesium sulfate, and vacuum-fractionated, yielding 7.4 g of a colorless viscous liquid, b.p. 124-128°/5 mm, which slowly crystallized out. Crystallization was appreciably

precipitated by addition of ligroin. After six crystallizations, 2.9 g of the second isomer of 4-butyldecahydro-1,2-dimethyl-4-quinolinol (VI) was obtained in the form of colorless needles, m.p. 98-99°.

Found %: C 75.55, 75.45; H 12.25, 12.25
$C_{15}H_{29}ON$. Calculated %: C 75.25; H 12.21
Found %: OH 7.29 (by Chugaev-Tserevitinov method)
$C_{15}H_{28}(OH)N$. Calculated %: OH 7.11.

Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII)

All syntheses with organolithium compounds were carried out in a current of dry nitrogen. Absolute ether (250 ml) and finely cut lithium (7.2 g) were introduced into a round-bottomed flask fitted with mechanical stirrer, reflux condenser, dropping funnel, thermometer and tube for passage of nitrogen, and a solution of bromobenzene (78 g) in absolute ether (75 ml) was added dropwise. When reaction had ceased, the mixture was heated at the boiling point of ether for two hours. To the phenyllithium so prepared, a solution of 60 g of octahydro-1,2-dimethyl-4(1H)-quinolone (b.p. 108-110°/4 mm, n_D^{20} 1.4975) in 75 ml of absolute ether was added dropwise with continuous stirring at −12° over a period of five hours. The reaction mixture was stirred with cooling for 40 minutes, and was then set aside overnight. On the next day it was stirred again for three hours at the temperature of boiling ether, and was then treated with 100 ml of water. The ether layer was separated, and the aqueous layer was saturated with caustic alkali and extracted with ether. The united ether solution was dried with magnesium sulfate, and the ether was driven off, when the residue partially crystallized out. It was filtered at the pump, yielding 40.7 g of crystals, m.p. 105-159°, from which, by fractional crystallization from acetone, 9.7 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) was isolated in the form of well-defined needles, m.p. 167.5-168°.

Found %: C 78.36, 78.51; H 9.86, 9.69
$C_{17}H_{25}ON$. Calculated %: C 78.71; H 9.71.

The hydrochloride of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol melted at 279-280° (from a mixture of alcohol and ether). Its picrate melted at 220-221° (from alcohol). In addition to the 9.7 g of high-melting isomer, the 40.7 g of crystals yielded also 25 g of a crystalline mixture of the isomers, m.p. 128-145°.

The mother liquor remaining after separation of the main crop (40.7 g) of crystals was evaporated down and set aside at room temperature. After three days crystallization had occurred. After three recrystallization from ligroin, 13.5 g of the low-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol was isolated in the form of a finely crystalline powder, m.p. 113-114°.

Found %: C 78.76, 79.02; H 9.81, 9.78
$C_{17}H_{25}ON$. Calculated %: C 78.71; H 9.71.

The picrate of the low-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol melted at 191-192° (from alcohol).

In this experiment, therefore, 9.7 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (m.p. 167.5-168°), 13.5 g of the low-melting isomer (m.p. 113-114°), and 25 g of a crystalline mixture of the two isomers (m.p. 128-145°) were isolated.

Decahydro-1,2,8a-trimethyl-4-phenyl-4-phenyl-4-quinolinol (IX)

A solution of 60 g of octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII) (b.p. 103-104°/3 mm; n_D^{20} 1.5018) in an equal volume of absolute ether was added dropwise with continuous stirring at −10° to phenyllithium prepared from 6.5 g of lithium and 72.3 g of bromobenzene dissolved in 300 ml of absolute ether. After the ketone had been added, stirring was continued with cooling (−5-10°) for one hour, then at room temperature for one hour, and finally on the next day at the temperature of boiling ether for four hours. Water (100 ml) was added, the ether layer was separated, and the aqueous layer was saturated with caustic alkali and extracted with ether. The united ether solution was dried with sodium sulfate, the ether was driven off, and the residue was vacuum-distilled, yielding 52.6 g of a viscous liquid, b.p. 155-159°/0.02 mm, which quickly crystallized out. Fractional crystallization from acetone yielded 12.4 g of the high-melting isomer of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol (IX) in the form of large needles, m.p. 164-165°.

Found %: C 79.23, 79.00; H 9.98, 10.03
$C_{18}O_{27}ON$. Calculated %: C 79.07; H 9.95.

The hydrochloride melted at 255-256° (from alcohol).

In addition 3.7 g of the low-melting isomer of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol was isolated in the form of small prisms, m.p. 130-132°.

Found %: C 79.30, 79.62, 79.21; H 9.74, 9.94, 10.13
$C_{18}H_{27}ON$. Calculated %: C 79.07; H 9.95

The hydrochloride melted at 284-285° (from alcohol).

The remaining portion of substance obtained (30.3 g) was a mixture of the two isomers of decahydro-1,2,8a-trimethyl-4-phenyl-4-quinolinol, m.p. 138-150°.

Octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI)

A solution of 9.5 g of hexahydro-1,2-dimethyl-1,5H-pyrindin-4(1H)-one (X) (b.p. 85-87°/2 mm; n_D^{20} 1.4915) in 10 ml of absolute ether was added dropwise with stirring at −12° over a period of one hour to phenyllithium prepared from 1.2 g of lithium and 13.3 g of bromobenzene in 100 ml of absolute ether. The reaction mixture was stirred for one hour with cooling, for one hour at room temperature, and for three hours on the next day at the boiling point of ether. The product was hydrolyzed with water (20 ml), the ether layer was separated, and the aqueous layer was saturated with solid caustic alkali and extracted with ether. The united ether solution was dried with sodium sulfate, the ether was driven off, and the residue was vacuum-fractionated, yielding 9.2 g of octahydro-1,2-dimethyl-4-phenyl-1,5H-pyrindin-4-ol (XI) in the form of a viscous liquid, b.p. 147-151°/0.07 mm; n_D^{20} 1.5474; d_4^{20} 1.0613. Found MR 73.24; Calculated MR 73.55.

Found %: C 78.56, 78.42; H 9.38, 9.46
$C_{16}H_{25}ON$. Calculated %: C 78.32; H 9.44.

Tetradecahydro-1,2-dimethyl-4-phenylbenzo [g or h] quinolin-4-ol (XIII or XIIIa)

A solution of 9 g of dodecahydro-1,2-dimethylbenzo[g or h] quinolin-4-(1H)-one (XII or XIIa) (b.p. 142-143°/3 mm; n_D^{20} 1.5210) in 15 ml of absolute ether was added dropwise with stirring at −12° to phenyllithium prepared in a round-bottomed flask from 1.35 g of lithium and 15 g of bromobenzene in 100 ml of absolute ether. The reaction mixture was stirred for one hour with cooling and for three hours on the next day at the boiling point of ether; it was then cooled, and decomposition was effected by addition of 20 ml of water. The ether layer was separated, and the aqueous layer was saturated with solid caustic alkali and extracted with ether. The united ether solution was dried with sodium sulfate, ether was distilled off, and the residue was vacuum-fractionated, yielding 9.7 g of tetrahydro-1,2-dimethyl-4-phenylbenzo[g or h]quinolin-4-ol (XIII or XIIIa), b.p. 167-172°/0.02 mm, which solidified to a glass-like mass in the receiver.

Found %: C 80.34, 80.39; H 10.08, 9.89
$C_{21}H_{31}ON$. Calculated %: C 80.45; H 9.96.

Decahydro-1,2-dimethyl-4-quinolinol (XIV)

a) A solution of 24 g of octahydro-1,2-dimethyl-4 (1H)-quinolone (b.p. 107-108°/4 mm; n_D^{20} 1.4980) in 470 ml of alcohol was placed in a round-bottomed flask. The solution was stirred continuously, and sodium (42 g) was added in small pieces over a period of 90 minutes, after which the reaction mixture was stirred further for two hours. The solution was acidified with 20% hydrochloric acid (300 ml), and the precipitate of sodium chloride that formed was filtered off and washed with hot alcohol. The filtrate was evaporated down under reduced pressure to 150-200 ml, and the base was liberated by addition of solid caustic alkali and extracted with ether. The ether solution was dried with potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled, yielding 15.4 g of decahydro-1,2-dimethyl-4-quinolinol in the form of a colorless viscous liquid having a feeble amine odor, b.p. 114-115.5° at 2 mm.

Found %: C 71.82, 72.07; H 11.74, 11.50
$C_{11}H_{21}ON$. Calculated %: C 72.07; H 11.54
Found %: OH 9.18 (by Chugaev-Tserevitinov method)
$C_{11}H_{20}(OH)N$. Calculated %: OH 9.27

b) A solution of 7.9 g of octahydro-1,2-dimethyl-4(1H)-quinolone (b.p. 107-108°/3 mm; n_D^{20} 1.4980) in 50 ml of alcohol was placed in an autoclave, and 0.3 g of a nickel catalyst was added. The substance was hydrogenated under 90 atm at 150° for 30 minutes. The catalyst was filtered off, the alcohol was distilled off, and the residue was vacuum-distilled, yielding 5.7 g of decahydro-1,2-dimethyl-4-quinolinol (XIV) in the form of a colorless viscous

liquid, b.p. 124-126.5° 4 mm.

Found %: OH 9.03, 8.96 (by Chugaev-Tserevitinov method)

$C_{11}H_{20}(OH)N$ Calculated %: OH 9.27

Acetic Ester of the High-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XV)

A solution containing 5 g of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (VII) (m.p. 167.5-168°), 20 ml of acetic anhydride, and 20 ml of pyridine was heated under reflux for eight hours at 140°. The pyridine and excess of acetic anhydride were driven off under the vacuum from a water pump, and to the residue a saturated solution of potassium carbonate was added to alkaline reaction (20 ml). The product was extracted with ether, and the ether extract was dried with magnesium sulfate. The residue after removal of ether crystallized out completely. After being boiled with active charcoal in benzene and then recrystallized from ligroin, the acetic ester of the high-melting isomer of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol obtained in this way melted at 122-123°.

Found %: C 75.85, 76.07; H 9.19, 9.17

$C_{17}H_{27}O_2N$. Calculated %: C 75.71; H 9.02.

By the action of dry hydrogen chloride on an ethereal solution of the base, the hydrochloride of the acetic ester of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol was obtained. After recrystallization from acetone it melted at 241-242°.

Acetic Ester of the Low-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XV)

A solution containing 1 g of the α-phenyl alcohol (m.p. 112-114°), 3 ml of acetic anhydride, and 3 ml of pyridine was heated at 140° for five hours. The pyridine and acetic anhydride were driven off, and the residue was diluted with 7 ml of water, saturated with potassium carbonate, and extracted with ether. The ether extract was dried with magnesium sulfate, and the liquid residue remaining after removal of ether was converted into its hydrochloride. The hydrochloride, which was obtained in the first place as an oil, was converted into a powder when rubbed out under absolute ether. After being reprecipitated twice from absolute alcohol by absolute ether, the hydrochloride was obtained in the form of crystals (0.3 g), m.p. 225-225.5°.

Found %: C 66.20, 66.31; H 8.57, 8.46; Cl 10.16, 10.57

$C_{19}H_{28}O_2NCl$ Calculated %: C 67.53; H 8.36; Cl 10.49.

Propionic Ester of the High-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XVI)

a) A solution containing 10 g of the α-phenyl alcohol VII of m.p. 167.5-168°, 35 ml of propionic anhydride, and 35 ml of pyridine was heated under reflux at 140-150° for eight hours. The pyridine and excess of anhydride were driven off, and to the residue 30 ml of saturated potassium carbonate solution and then dry potassium carbonate were added. The product was extracted with ether, and the ether extract was dried with magnesium sulfate. The product after removal of ether was converted into its hydrochloride (10.5 g of crude hydrochloride). Two reprecipitations from a mixture of absolute alcohol and ether yielded 7.5 g of the propionic ester of decahydro-1,2-dimethyl-4-phenyl-4-quinolinol hydrochloride, m.p. 230-231°.

Found %: C 68.35, 68.44; H 8.63, 8.60; Cl 9.95, 9.92

$C_{21}H_{32}O_2NCl$. Calculated %: C 68.22; H 8.59; Cl 10.08.

b) A drop of sulfuric acid was added to a solution of 1.4 g of the α-phenyl alcohol VII of m.p. 165-166.5° in 15 ml of propionic anhydride, and the mixture was heated for four hours at 100°. The propionic anhydride (excess) was driven off, and the residue was diluted with 2 ml of water and saturated with sodium carbonate. The base was extracted with ether, and the ether extract was dried with magnesium sulfate, distilled to remove ether, and vacuum-distilled, yielding 0.8 g of viscous yellow liquid, b.p. 140°/0.02 mm, which crystallized out when rubbed. Two recrystallizations from ligroin yielded 0.6 g of crystals, m.p. 165-166.5°. In admixture with the original α-phenyl alcohol it showed no depression of melting point.

Propionic Ester of the Low-melting Isomer of Decahydro-1,2-dimethyl-4-phenyl-4-quinolinol (XVI)

A solution of 6.8 g of the α-phenyl alcohol (VII) of m.p. 113-115° in 21 ml of propionic anhydride and 16 ml of pyridine was heated at 145-150° for nine hours. The excess of propionic anhydride and pyridine were driven off under the vacuum from a water pump, and the residue was diluted with 20 ml of water and saturated with potassium carbonate until a slurry was formed. The base was carefully extracted with ether, dried with magnesium sulfate, and, after distillation, converted into the hydrochloride. The oily hydrochloride so obtained was dissolved in the least possible amount of absolute alcohol, and absolute ether was added to the solution until a turbidity was produced. After prolonged standing, 1.3 g of crystals of the hydrochloride of the propionic ester of the low-melting isomer of decahydro-1,2-dimethyl-4-quinolinol, m.p. 195-196°, was obtained.

Found %: C 68.13, 68.17; H 8.63, 8.54
$C_{20}H_{32}O_2NCl$. Calculated %: C 68.22; H 8.59

Benzoic Ester of 4-Ethynyldecahydro-1,2-dimethyl-4-quinolinol (XVII)

A solution of 7 g of the acetylenic alcohol II of b.p. 129-131°/3mm in 35 ml of pyridine and 16 ml of benzoyl chloride was heated under reflux in a boiling water bath for four hours. The pyridine and excess of benzoyl chloride were distilled off, and ether was added to the residue; no crystals appeared. The residue was dissolved in 30 ml of water, the base was carefully separated with cooling by means of sodium carbonate, and was then extracted with ether, the extract being neutralized with carbon dioxide and dried with magnesium sulfate. The residue after removal of ether was a dark-colored resin containing crystals. These were extracted and recrystallized from benzene. The product was 0.39 g of the benzoic ester of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol, m.p. 174-175°.

Found %: C 76.87, 76.82; H 8.32, 8.29
$C_{25}H_{35}O_2N$. Calculated %: C 77.07; H 8.09

The residual mass was a nondistilling resin. It was not found possible to obtain the hydrochloride of the benzoic ester of 4-ethynyldecahydro-1,2-dimethyl-4-quinolinol in a crystalline form.

Benzoic Ester of Decahydro-1,2-dimethyl-4-quinolinol (XVIII)

A solution of 4 g of decahydro-1,2-dimethyl-4-quinolinol (XIV) (b.p. 124-125°/4 mm) in 10 ml of benzoyl chloride was saturated with gaseous hydrogen chloride and heated at 100° for five hours. The excess of benzoyl chloride was driven off in a water bath under the vacuum from a water pump. The residue was extracted with ether, and was then diluted with 12 ml of water. Potassium carbonate was added, and the base was extracted with ether. The ether extract was dried with magnesium sulfate, the ether was distilled off, and the residue was distilled, yielding 2.8 g of the benzoic ester of decahydro-1,2-dimethyl-4-quinolinol in the form of a very viscous liquid, b.p. 154-156°/2 mm.

Found %: C 74.83, 74.67; H 8.31, 8.21
$C_{18}H_{25}O_2N$. Calculated %: C 75.22; H 8.75

It was not found possible to isolate the hydrochloride of the benzoic ester of decahydro-1,2-dimethyl-4-quinolinol in a crystalline form.

Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninonitrile (XIX)

a) Hydrochloric acid (12 ml, 1 : 1) was added to 10 g of octahydro-1,2,8a-trimethyl-4(1H)-quinolone (VIII) (b.p. 103-104°/3 mm; n_D^{20} 1.5020), and with stirring and cooling to 0° a solution of 4 g of potassium cyanide in 6 ml of water was added. The medium became weakly alkaline, and after a few minutes crystals appeared. The reaction mixture was stirred further for two hours at room temperature. The crystals were extracted with ether, and the ether solution was dried with sodium sulfate. The ether was driven off, and the residue, a thick oil, partially crystallized out after a short time, yielding 1.6 g of crystals, m.p. 102-107°. Melting point after recrystallization from acetone 118-120°. The mother liquor was distilled, yielding 4.9 g of the original quinolone, b.p. 102-105°/3 mm, n_D^{23} 1.5000.

Analysis of crystals m.p. 118-120°:
Found %: N 12.60, 12.54
$C_{13}H_{22}ON_2$. Calculated %: N 12.60

b) Hydrochloric acid (16 ml, 1 : 1) was added to 10 g octahydro-1,2,8a-trimethyl-4 (1H)-quinolone (VIII) (b. p. 113-114° at 3 mm; n_D^{20} 1.5020), and with stirring and cooling to 0° 4 g of potassium cyanide was added. Stirring was continued for 90 minutes. The medium was acid in reaction, and a solution of potassium carbonate was added to neutral reaction; dry potassium carbonate was then added. The product was extracted with ether, and the ether extract was dried with sodium sulfate. The ether was driven off, and the residue partially crystallized out, yielding 3.2 g of crystals of the cyanohydrin, m. p. 102-107°. After recrystallization from acetone the substance melted at 118-120°.

Methyl Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI)

Concentrated hydrochloric acid (15 ml) was added to 3 g of the cyanohydrin, and the solution was heated in a boiling water bath for ten hours. The hydrochloric acid was evaporated off in a porcelain dish on a water bath. Absolute alcohol was added to the dry residue, and the precipitate of ammonium chloride was filtered off. The alcohol was driven off, yielding as residue the hydrochloride of decahydro-4-hydroxy-1,2,8a-trimethylcinchoninic acid (XX) in the form of a viscous liquid.

To the hydrochloride of the hydrolysis product (XX), 20 ml of absolute methanol was added, and dry hydrogen chloride was passed through the mixture at the boiling point of the alcohol for two hours. The methanol and hydrogen chloride were removed under reduced pressure, and to the residue, a thick dark-colored liquid, 10 ml of water and some potassium carbonate were added. The base was extracted with ether, and the ether extract was dried with sodium sulfate. The residue after removal of ether was 1.6 g of crystalline methyl decahydro-4-hydroxy-1,2,8a-trimethylcinchoninate (XXI), which melted, after two recrystallizations from acetone, at 138-139°.

Found %: C 65.76, 65.56; H 9.93, 9.82

$C_{14}H_{25}O_3N$. Calculated %: C 65.84; H 9.86.

Methyl 4-Benzoyloxydecahydro-1,2,8a-trimethylcinchoninate (XXII)

Benzoyl chloride (5 ml) was added to 1 g of the hydroxy ester XXI. The reaction was carried out for five hours in a boiling water bath, and for one hour at 130-140°. The benzoyl chloride was removed in a boiling water bath under the vacuum from a water pump. Water (10 ml) was added to the viscous dark-colored residue. Residual benzoyl chloride was extracted with ether. The base was liberated with potassium carbonate and extracted with ether. The ether solution was dried with sodium sulfate. The ether was driven off, and the residue crystallized out. The product after recrystallization from acetone, was 0.15 g of substance of m.p. 256-257°.

Found %: C 69.14, 69.15; H 7.95, 8.07

$C_{21}H_{27}O_4N$ Calculated %: C 70.19; H 8.07

SUMMARY

1. Various alcohols of the decahydroquinoline, perhydro-1-pyrindine, and perhydrobenzoquinoline series have been synthesized.

2. Six esters of the decahydroquinoline series have been prepared.

3. Decahydro-4-hydroxy-1,2,8a-trimethylcinchoninonitrile, the corresponding acid, and its esters have been synthesized.

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COMMUNICATION 55. APPLICATION OF INTERCHAIN EXCHANGE REACTIONS IN LINEAR POLYCONDENSATION PROCESSES

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It has been shown in a series of investigations in our laboratory [1] that the linear-polycondensation reaction is a very complex equilibrium process involving both synthetic and degradational reactions. We have shown also, working with polyesters [2] and polyamides [3], that the linear-polycondensation reaction leads to the formation of products having a comparatively low degree of polydispersity, which is contrary to the predictions of the mechanical theories of Flory [4] and Schulz [5]. The main cause of the equalization of chain lengths in the polymer formed is the occurrence of exchange reactions between the growing polymer chains – reactions of interchain exchange, consisting in interaction between chains of different lengths involving not only active end groups, but also the bonds between individual structural units of the macromolecule. These two types of reactions may be represented in a general way by the following equations:

For polyesters –

$$H(ORO-COR'CO)_xOH + H(ORO-COR'CO)_yOH \rightleftarrows H(ORO-COR'CO)_mOH + H(ORO-COR'CO)_nOH. \quad (I)$$

For polyamides –

$$H(NHRNH-COR'CO)_xOH + H(NHRNH-COR'CO)_yOH \rightleftarrows H(NHRNH-COR'CO)_mOH + H(NHRNH-COR'CO)_nOH.$$

where $m + n = x + y$. (Ia)

The processes represented by these equations (I and Ia) proceed for these classes of compounds by acidolysis, alcoholysis, and aminolysis reactions and involve the reaction of an end group of one of the reacting molecules with the ester, amide, or other linkage of another molecule.

However, as we have shown in a number of cases, interchain exchange may proceed also by the mechanism of transesterification, transamidation, or the like, i.e. by reaction between ester, amide, or other linkages of one molecule with similar linkages in another molecule, as shown in Equations II and IIa:

$$H(ORO-COR'CO)_x \overset{\vdots}{-} (OROCOR'CO)_yOH + HO(COR'CO-ORO)_m \overset{\vdots}{-} (COR'CO-ORO)_nH \rightleftarrows$$
$$\rightleftarrows H(ORO-COR'CO)_x-(OROCOR'CO)_mOH + HO(COR'CO-ORO)_y-(COR'CO-ORO)_nH, \quad (II)$$

where $x + y \neq x + m$.

$$H(NHRNH-COR'CO)_x \overset{\vdots}{-} (NHRNH-COR'CO)_yOH + HO(COR'CO-NHRNH)_m \overset{\vdots}{-} (COR'CO-NHRNH)_nH \rightleftarrows$$
$$\rightleftarrows H(NHRNH-COR'CO)_x-(NHRNH-COR'CO)_mOH + HO(COR'CO-NHRNH)_y-(COR'CO-NHRNH)_nH. \quad (IIa)$$

In a series of previous investigations we have shown that acidolysis, aminolysis, and alcoholysis lead to the degradation of polyamides and polyesters owing to scission of ester and amide linkages in presence of free carboxyl [6, 7, 8], amino [8], or hydroxyl [9] groups, and also of the ester linkages of other molecules [10]. The kinetics of these exchange reactions were studied in great detail for low-molecular-weight esters, alcohols, and acids [11].

The object of the present investigation was the experimental proof of the reaction schemes represented above for the interchain exchange processes in cases for which alcoholysis, acidolysis, and aminolysis should lead not to degradation, but to the synthesis of polyesters and polyamides having quite definite degrees of heterogeneity, corresponding to polycondensation equilibrium.

We have studied a number of samples of the synthesis of polyesters by the alcoholysis reaction. It was found, for example, that formation of polyethylene adipate proceeded readily when ethylene glycol reacted with dialkyl (dibutyl and diethyl) adipates:

$$x\,ROCO(CH_2)_4COOR + xHOCH_2CH_2OH \longrightarrow \cdots - CO(CH_2)_4CO - OCH_2CH_2O - \cdots + (2x-1)\,ROH \qquad (III)$$

This reaction proceeds more rapidly in presence of acid or alkaline catalysts, but proceeds at an appreciable rate even in their absence. We obtained a polymer of this type also by prolonged heating of bis(2-hydroxyethyl) adipate:

$$x\,HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH \rightleftharpoons \cdots - OCH_2CH_2O - CO(CH_2)_4CO - \cdots + x\,HOCH_2CH_2OH \qquad (IV)$$

The interaction of polyester chains among themselves was verified by us also by studying the fractional composition of polyesters obtained by different methods. One of these (Sample No. 30) was prepared by heating adipic acid with ethylene glycol under the usual polycondensation conditions. The other (Sample No. 31) was prepared by prolonged heating (42 hours) of a narrow fraction of Sample No. 30 having a molecular weight of 1100.

Both polyester samples were separated into narrow fractions by a fractional-precipitation method [12]. The figure shows the molecular-weight distribution curves for Samples No. 30 and 31 of polyester. It will be seen that the distribution curves of the two samples are similar to each other, , in spite of the fact that Sample No. 30 was obtained by the polycondensation of the original substances, and Sample No. 31 was formed as the result of interchain exchange within a narrow fraction of the polymer (indicated on the figure by broken lines). The shift that has occurred in the maximum is to be explained by an increase in the degree of completeness of the reaction. The reaction of interchain exchange leads, therefore, to formation of a polycondensate having a degree of polydispersity corresponding to a state of equilibrium.

Alcoholysis of polyamide chains by hydroxy compounds does not occur in absence of catalysts. This is confirmed by the fact that prolonged heating of the diamide of adipic acid with ethylene glycol under polycondensation conditions does not lead to polyester formation. On the other hand, aminolysis of ester linkages occurs readily and leads to the formation of polyamides. We established this fact by studying the reaction of dibutyl adipate with 1,6-hexanediamine. When 1,6-hexanediamine is heated with excess of dibutyl adipate, the formation occurs of polyamides having butoxyl end groups:

$$(x+1)C_4H_9O - CO(CH_2)_4CO - OC_4H_9 + xH_2N(CH_2)_6NH_2 \longrightarrow$$

$$\longrightarrow C_4H_9O - CO(CH_2)_4CO - [NH(CH_2)_6NHCO(CH_2)_4CO]_x OC_4H_9 + 2C_4H_9OH \qquad (V)$$

Polyamide synthesis by acidolysis of amide linkages proceeds readily in absence of a catalyst. Thus, when N,N-hexamethylenebisacetamide is heated with adipic acid under polycondensation conditions, polyhexamethyleneadipamide is formed with elimination of acetic acid:

$$xCH_3CO - NH(CH_2)_6NH - COCH_3 + xHOCO(CH_2)_4COOH \rightleftharpoons \cdots - NH(CH_2)_6NH - CO(CH_2)_4CO - \cdots + (2x-1)CH_3COOH \qquad (VI)$$

Interchain exchange by the transamidation reaction (Equation IIa) proceeds rapidly only in presence of a catalyst. We have found that diethyl adipate does not react with N,N'-hexamethylenebisacetamide at 200-210° under the usual polycondensation conditions, but in presence of an aqueous solution of p-toluenesulfonic acid reaction occurs under the same conditions with formation of a polyamide and elimination of ethyl acetate.

EXPERIMENTAL

Synthesis of Bis(2-hydroxyethyl) Adipate

A mixture of 7.2 g (0.05 mole) of adipic acid and 17.4 g (0.28 mole) of ethylene glycol was heated under polycondensation conditions for nine hours at 180°. Samples were taken at known intervals of time and their carboxyl contents were determined. Reaction was discontinued when 99.5% of the carboxyl groups had entered into reaction. A mixture of water and glycol (3.4 g) was driven off, and then at 150° 8.0 g of distillate was obtained at a pressure of 2 mm. The total amount of distillate was 11.4 g, of which 1.8 g was water and 9.6 g was unchanged ethylene glycol, b.p. 195-196°. The residue in the flask (11.5 g) was a viscous liquid that did not boil under reduced pressure (2 mm) when heated to 250°. It was difficultly soluble in benzene, but readily soluble in alcohol.

The product (10 g) was dissolved in alcohol (30 ml), and the solution was diluted with water (100 ml). An oily layer of polyester formed at the top, and it was poured off, it solidified to a white greasy substance, m.p. 26-29° (1.1 g). The aqueous-alcoholic solution was evaporated to constant weight at 10 mm and 56°.

	Found %:	H 7.35, 7.40, C 51.61, 54.68
$C_{10}H_{18}O_6$	Calculated %:	H 7.73, C 51.27
	Acid number 1.5.	

Determination of hydroxyl groups by Verley's method [3]:

In a control experiment 20 ml of the acetylating mixture required 35.2 ml of 0.1 N alkali (factor 1.05). In a determination on 0.1692 g of the substance 22.26 ml of alkali was required. In a determination on 0.1748 g of the substance 21.0 ml of alkali was required. These figures yield molecular weights of 226 and 230 respectively.

Found: M 230

$C_{10}H_{18}O_6$. Calculated: M 232

The product therefore corresponds in elementary analysis and molecular weight to bis(2-hydroxyethyl) adipate

Alcoholysis of Esters

Synthesis of a polyester from bis(2-hydroxyethyl) adipate. The bis (2-hydroxyethyl) ester (7 g) was heated under polycondensation conditions for four hours at 180° and 10-12 mm. During the heating a heavy liquid slowly distilled over; it was found to be ethylene glycol (1.7 g). The residue solidified to a hard white mass, m.p. 38-40°. Viscosity measurements in benzene solution(8.6 g/liter): η_{sp} 0.084, $[\eta]$ 0.0097. M 1800.

Reaction of diethyl and dibutyl adipates with ethylene glycol. Equimolecular amounts of dialkyl adipate and ethylene glycol were heated together under polycondensation conditions both with and without catalysts.

p-Toluenesulfonic acid and sodium ethoxide were used as catalysts (1% on the total weight of the original substances). The amount of alcohol that separated in the course of the reaction was determined by trapping it in a graduated receiver followed by tubes containing freshly calcined calcium chloride. The losses of alcohol in the apparatus, as determined by checks on pure alcohol, were 0.05 - 0.06 g. The results of the experiments are given in Table 1.

TABLE 1

Synthesis of Polyesters from Dialkyl Adipates and Ethylene Glycol

Expt. No.	Starting substances		Reaction conditions		Degree of completion of reaction	Mol. wt.*	Notes
	Amt. of ethylene glycol (g)	Amt. of ester (g)	temp. (°C)	time (hr)			
1	5.0	Diethyl adipate 16.2	160-90	5	0.32	460	No catalyst
2	3.25	" " 10.6	160-90	5	0.63	900	1% p-toluenesulfonic acid
3	3.1	" " 10.1	170-95	7	0.73	1260	1% sodium ethoxide
4	3.1	" " 10.1	160-95	6	0.73	1250	Ditto
5	3.1	Dibutyl adipate 12.9	180-200	6	0.50	700	Ditto

Aminolysis of Esters

Reaction of dibutyl adipate with 1,6-hexanediamine. A mixture of 4.6 g (0.01 mole + 75% excess) of dibutyl adipate and 1.16 g (0.01 mole) of 1,6-hexanediamine was heated in a Claisen flask for three hours at a bath temperature of 225-230°. Reaction began at 180°, and distillation of butyl alcohol had practically ceased after three hours. The temperature rose to 225° during the first hour. The distillate (1 g) consisted of butyl alcohol containing a certain amount of free base, which was determined by titration with sulfuric acid in presence of Methyl Orange. The amount of 0.1 N sulfuric acid required was 0.6 ml per g; the amount of diamine in the distillate was 0.007 g, i.e. 0.6% of the diamine taken.

The reaction product was a white, amorphous mass, m.p. 190-200°, insoluble in water and ether. Boiling absolute methanol dissolved about 40% of the total amount. The residue was soluble only in phenols and formic acid, and was precipitated from them by alcohol and water respectively. M.p. 205-207°.

* The viscometric molecular weight was determined in all cases on samples that had been washed with water, washed with ether, and dried to constant weight. The viscosity measurements were carried out on benzene solutions.

Found %: N 9.04; 8.89

$C_{64}H_{92}O_{16}N_6$ Calculated %: N 8.98

Found %: H 10.31; 10.22; C 63.95; 63.93

$C_{68}H_{94}O_{16}N_8$ Calculated %: H 9.92; C 64.05

The molecular weight according to the elementary composition was 936, and as determined from the viscosity of a solution in m-cresol, 1000. According to its elementary composition, therefore, the product corresponded to a polyamide containing 3 residues of 1,6-hexanediamine, 4 adipic acid residues, and 2 butoxyl groups, i.e., to a polyamide having a degree of polycondensation of 7.

When the alcoholic extract of the reaction product was cooled, a white, amorphous precipitate formed, which melted, after recrystallization from 95% alcohol, at 108-112°. Repeated recrystallization from alcohol had no effect on the melting point.

Its mean molecular weight by the formula was 585. Its molecular weight determined from the viscosity of its solution in m-cresol was 630.

Acidolysis of Amides

Reaction of N,N'-hexamethylenebisacetamide with adipic acid. A mixture of 4 g (0.02 mole) of N,N'-hexamethylenebisacetamide (m.p. 124-125°) and 2.93 g (0.02 mole) of adipic acid was heated in a Claisen flask in an atmosphere of dry nitrogen (purified from oxygen) for two hours at 180° and two hours at 210-215°. During the reaction 0.25 g of acetic acid was distilled off. The residue in the flask rapidly solidified to a white mass, m.p. 145-147°. After being ground, repeatedly washed with water, and then dried, the product (4.6 g of white powder) melted at 242-245°. In admixture with polyhexamethyleneadipamide it melted at 243-246°. Its specific viscosity at 7.2 g per liter was 0.16; molecular weight 2600.

Reaction of N,N'-hexamethylenebisacetamide with diethyl adipate. 1) A mixture of 3.4 g of N,N'-hexamethylenebisacetamide (m.p. 124-125°) and 3.5 g of diethyl adipate (b.p. 102-104°/3 mm; acid number 0.004) was heated in a current of nitrogen for four hours at 200-210°. There was a partial darkening of the reaction mixture. Nothing condensed in a receiver provided, but an odor of acetic acid could be detected. The loss in weight of the reaction mixture was 0.1 g. The product melted at 110-116°; recrystallization from dry benzene yielded 3.1 g of a white crystalline substance, m.p. 124-125°. In admixture with the original N,N'-hexamethylene-bisacetamide it melted at 124-125°.

2) The experiment was repeated, but before the heating a solution of 0.1 g of p-toluenesulfonic acid in 1 ml of water was introduced into the reaction flask. During the reaction 1.4 g of a liquid smelling of ethyl acetate distilled over, but it did not separate from the water as a layer. The residue in the flask was a hard, white substance, m.p. 140-150°. Repeated washing with water yielded 3.5 g of a white powder, m.p. 244-247°, which appeared to be polyamide, but which was not investigated further.

Amide-alcoholysis reaction. The diamide of adipic acid, dried to constant weight (14.4 g, i.e., 0.1 mole; m.p. 220°) was placed in a round-bottomed flask, and 31 g of carefully dried ethylene glycol was added. The mixture was heated under reflux for three hours at 200°, and was then cooled. Absolute alcohol (50 ml) was added, and the precipitate that formed was separated, washed on the filter with absolute alcohol, and dried to constant weight (14.1 g; m.p. 219-220°). In admixture with the original diamide it melted at 219-220°.

Synthesis of Polyester No. 30

A mixture of 58.0 g of adipic acid and 24.8 g (1% excess over equimolecular amount) of ethylene glycol was heated in a current of dry nitrogen for 6 hr. 20 min. at 160° and 1 hr. 30 min. at 180°. In the course of the reaction 12.5 g of water distilled off. The residue in the flask was a white solid, m.p. 40-41°, 70 g; it dissolved readily in benzene, chloroform, and dioxane. The degree of completion of the reaction, according to the amount of water separated, was p = 0.87. The molecular weight according to the water liberated, was 770, and according to cryoscopic determination in benzene solution, 730. The specific viscosity of a benzene solution of concentration 10.32 g per liter was 0.0575. The viscometric molecular weight was 1070.

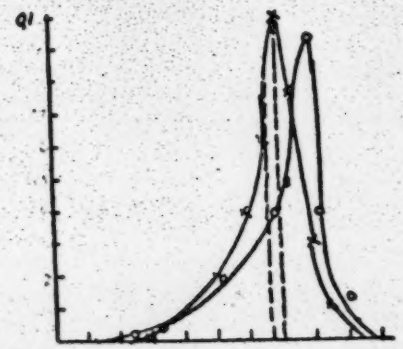

TABLE 2

Fractional Composition of Polyester No. 30

Fraction No.	Weigh of fraction(g)	Losses (g)	Total weight (g)	Molecular weight
I	0.98	0.19	1.17	1430
II	1.25	0.19	1.44	1260
III	1.18	0.28	1.46	1220
IV	3.25	0.66	3.91	1120
V	1.43	0.34	1.77	860
VI	0.16	–	0.16	500
Not fractionated	8.25	1.66	9.91	1070
Calculated mean*	–	–	–	1130

* Calculation of the mean molecular weight of the unfractionated mixture was performed by the formula $Mm = \Sigma f_x M_x$, where f_x is the proportion by weight of a fraction, and M_x is the molecular weight of this fraction.

Fractionation of Polyester No 30

1. The polyester (10 g) was dissolved in 500 ml of dry benzene, and by fractional precipitation by means of light petroleum ether, six fractions were separated by the method described previously [12]. The results of the fractionation are given in Table 2 and in the figure.

2. Polyester No. 30 (47 g) was separated into fractions by the method indicated above. One of these fractions (16 g), which had a molecular weight of 1100, was again treated to free it from low- and high-molecular weight polymer, and the fraction so obtained (10.85 g) had a mean molecular weight of 1100.

Further attempts to separate low- and high-molecular weight impurity from this fraction were without result.

Preparation of Polyester No. 31

The fraction of polyester No. 30 having a molecular weight of 1100 (10.15 g) was heated in a sealed tube at 170° for 42 hours. In external appearance the reaction product did not differ from the original polyester.

Some of the polyester so obtained (9.5 g) was dissolved in 500 ml of benzene, and six fractions were separated by fractional precipitation with petroleum ether. The results are given in Table 3. The curve for the distribution of fractions of different molecular weights is given above in the figure.

TABLE 3

Fractional Composition of Polyester No. 31

Fraction No.	Weight of fraction (g)	Losses (g)	Total weight (g)	Molecular weight
I	1.10	0.28	1.38	1550
II	1.22	0.23	1.45	1320
III	1.33	0.19	1.52	1290
IV	3.06	0.57	3.63	1150
V	0.89	0.34	1.23	750
VI	0.17	–	0.17	450
Not fractionated	7.77	1.61	9.38	1200
Calculated mean	–	–	–	1190

SUMMARY

1. A study has been made of interchain-exchange reactions, leading to the synthesis of polyesters and polyamides, in compounds having amide and ester linkages.

2. It has been shown that, in presence of free hydroxyl, carboxyl, or amino groups, exchange reactions of the alcoholysis, acidolysis, or aminolysis types respectively occur at ester linkages. Amide linkages are broken only by amino and carboxyl groups; they are stable toward hydroxyl groups.

3. It has been found that no exchange reaction occurs between diethyl adipate and N,N'-hexamethylenebisacetamide in absence of catalyst; it occurs only in presence of an acid catalyst.

4. It has been shown that a narrow fraction of a polyester undergoes considerable change when subjected to prolonged heating: interchain exchange reactions occur, resulting in the formation of a more heterogeneous material, the distribution curve for which is similar to that of the original unfractionated polyester obtained by the polycondensation of adipic acid withethylene glycol.

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* See Consultants Bureau Translation, p. 125.

COMMUNICATION 59. STEREOCHEMISTRY OF α-METHYLSTYRENES IN ITS RELATION TO THEIR TENDENCY TO UNDERGO POLYMERIZATION

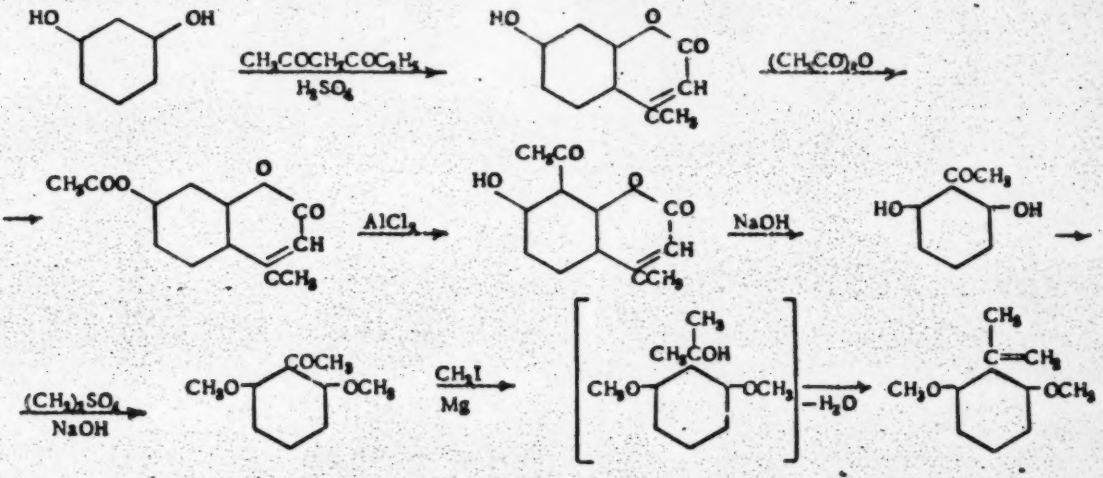
V. V. Korshak and N. G. Matveeva

As we have shown in the preceding communication, meta and para substituents in the styrene molecule have no steric-hindrance effect on the polymerization process; this is true also for a single substituent ortho to the vinyl group [1]. Even such a large substituent as the isopropyl group – as shown, for example, by the behavior of the 2,4,5-triisopropylstyrene that we prepared [1] – does not impede polymerization. But if there are two ortho substituents, the effects are much greater. We found that the nature of these substituents was important also. Thus in the case of the methoxyl group (2,6-dimethoxystyrene [1]), the ease of rotation and the small size of the oxygen atom results in an absence of steric hindrance, and this styrene derivative readily polymerizes; but the behavior of 4-tert-butyl-2,6-dimethylstyrene [2] shows that when the substituent is a methyl group great steric difficulties arise in the process of radical polymerization, which is practically inhibited, although the styrene derivative is still able to undergo ionic polymerization.

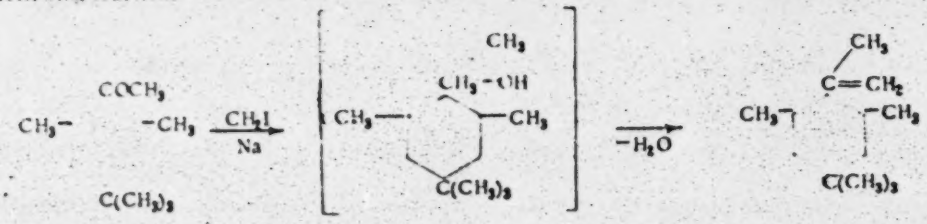
It was of great interest to consider the steric effects in ortho-disubstituted styrenes in their relation to the effects of substituents in the vinyl group. We have previously studied some unsymmetrical disubstituted ethylenes, and have shown that steric hindrance is considerable only for such large substituents as phenyl and cyclohexyl [3].

In this investigation we have studied the stereochemical effects occurring in certain 2,6-disubstituted α-methylstyrenes. For this purpose we synthesized 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene and investigated their ability to undergo polymerization. 2,6-Dimethoxy-α-methylstyrene was prepared by a long succession of reactions, which are shown schematically below.

The starting substance was 4-methylumbelliferone, which was prepared from resorcinol and acetoacetic ester in presence of concentrated sulfuric acid. Acetylation of 4-methylumbelliferone, Fries rearrangement, and hydrolysis of the product led to 2',6'-dihydroxyacetophenone, which was methylated with dimethyl sulfate, yielding 2',6'-dimethoxyacetophenone. This was converted by the action of methylmagnesium iodide into 2,6-dimethoxy-α,α,-dimetheybenzyl alcohol, which immediately underwent dehydration, yielding 2,6-dimethoxy-α-methylstyrene, a liquid of b.p. 136-138° at 26 mm.



4-tert-Butyl-α-2,6-trimethylstyrene was prepared from 4'-tert-butyl-2',6'-dimethylacetophenone by the following reactions:



Treatment of 4'-tert-butyl-2',6'-dimethylacetophenone with methyl iodide and sodium (Shorygen's reaction [5]) 4-tert-butyl-α,α,2,6-tetramethylbenzyl alcohol, which underwent dehydration in the course of isolation, yielding 4-tert-butyl-α,2,6-trimethylstyrene, a liquid of b.p. 124—125°/3 mm. Our attempts to prepare this substance with the aid of methylmagnesium iodide were not successful, for it was found that 4'-tert-butyl-2',6'-dimethylacetophenone did not react with methylmagnesium iodide and could be recovered unchanged after the treatment. It was thus possible to overcome the steric hindrance in this reaction only with the help of Shorygin's reaction.

The α-methylstyrenes obtained were submitted to various treatments in a search for ways of bringing about their polymerization. They were heated at 200° for 250 hours; heated for a long time in presence of benzoyl peroxide; subjected to the action of aluminum chloride; and irradiated for a long time with ultraviolet radiation from a quartz lamp. In no case, however, was any sign of polymerization detected. We were therefore forced to the conclusion that these α-methylstyrenes are completely unable to undergo polymerization.

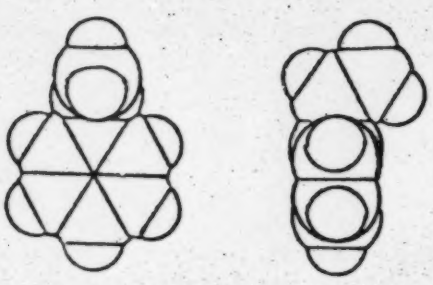


Fig. 1. Styrene.

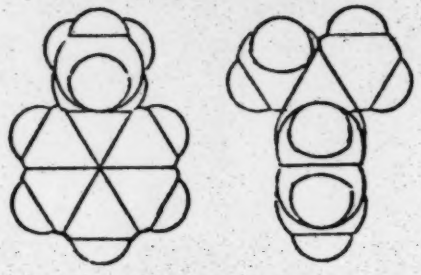


Fig. 2. α-Methylstyrene.

Examination of the spatial models of styrene and α-methylstyrene shown in Fig. 1 and 2 will make it clear that the presence of the α-methyl group gives rise to considerable steric effects that will impede the polymerization process. This results in loss of ability to undergo radical polymerization, but the ability to undergo ionic polymerization in presence of aluminum chloride, boron trifluoride, and other catalysts is still retained. In this respect α-methylstyrene closely resembles 4-tert-butyl-2,6-dimethylstyrene, in which, as we have already shown [2], steric hindrance due to the presence of two ortho-methyl groups again leads to loss of ability to undergo radical polymerization without loss in ability to undergo ionic polymerization. In Fig. 3 we show a spatial model of 4-tert-butyl-2,6-dimethylstyrene in which the considerable blocking effect due to the two methyl groups will be readily seen.

We have explained the retention by these compounds of ability to undergo ionic polymerization in terms of the difference between polar and nonpolar forces, for it is known that whereas polar forces are proportional to $1/r^3$, nonpolar forces vary as $1/r^{10}$, r being the distance between the particles. The polar forces arising in ionic polymerization are therefore able to act at a greater distance than the nonpolar forces that occur in radical polymerization, and it is not surprising that steric obstacles are more readily overcome in ionic polymerization [2].

When we compare these two compounds with the two compounds that we have now synthesized, 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene, spatial models of which are represented in Fig. 4 and 5, it is readily seen that in these compounds the steric hindrance has increased many times. This arises from the superposition of the screening and blocking effects arising from the two substituents. As a result, the steric obstacles

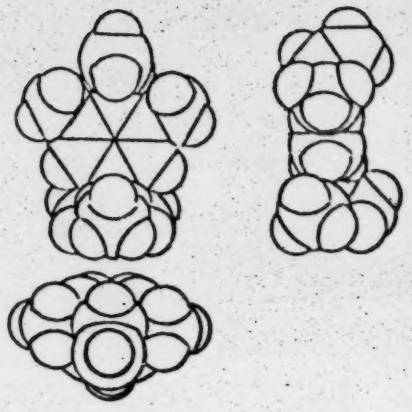


Fig. 3. 4-tert-Butyl-2,6-dimethylstyrene.

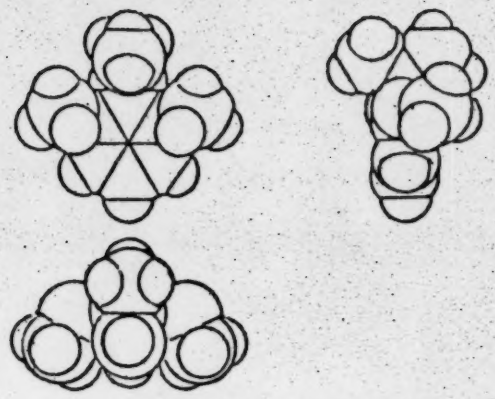


Fig. 4. 2,6-Dimethoxy-α-methylstyrene

become so great that they inhibit reaction not only with free radicals, but also with the ions present during ionic polymerization.

We may therefore conclude, on the basis of the behavior of these two ortho-substituted α-methylstyrenes, that even a small substituent, such as a methyl group, can create very great steric obstacles to the polymerization of disubstituted ethylene, when the second substituent is ortho-disubstituted phenyl. It follows that, as we have previously shown, stereochemical factors may hinder the polymerization not only of tetrasubstituted ethylenes [4] and of disubstituted ethylenes having two large substituents [5], but also of disubstituted ethylenes having one small and one large, ramified substituent.

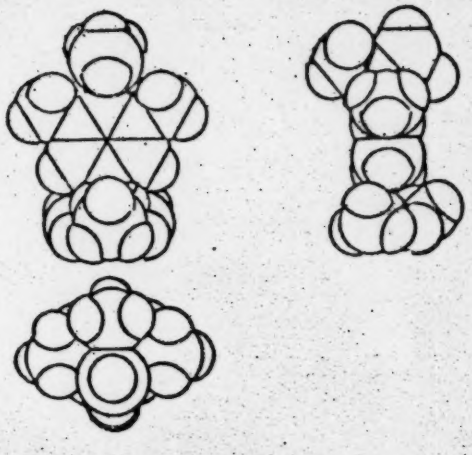


Fig. 5. 4-tert-Butyl-α,2,6-trimethylstyrene

EXPERIMENTAL

4-tert-Butyl-α,2,6-trimethylstyrene. 4'-tert-Butyl-2',6'-dimethylacetophenone (100 g), methyl iodide (210 g), and granulated sodium (48 g) in ether (250 ml) were introduced into a round-bottomed flask fitted with reflux condenser. As the beginning of the reaction was generally somewhat delayed, ethanol (1 ml) was added as primer. When reaction began to die down, the flask was heated in a water bath for one hour; it was then set aside overnight. The ether layer, containing suspended alkoxide, was carefully decanted from the sodium, and the residual sodium was shaken several times with ether, the ethereal suspension of alkoxide being poured off each time. The ether extracts were united, and the alkoxide was decomposed with water. The ether layer was separated in a separating funnel and then washed, first with water, then with dilute hydrochloric acid, and then again with water. The washed ether layer was dried with calcined sodium sulfate, the ether was distilled off, and the residue was vacuum-distilled. After three distillations 15.7 g (15.5%) of a substance of b.p. 124--125°/3 mm was obtained.

4-tert-Butyl-α,2,6-trimethylstyrene is a colorless viscous oil having an odor of turpentine, d_4^{20} 0.9489; n_D^{20} 1.5050; found MR 68.13. Calc. MR 68.62. It is readily soluble in organic solvents and insoluble in water.

Found %: C 88.20, 88.22; H 10.58, 10.61
Calculated %: C 89.03; H 10.96.

2,6-Dimethoxy-α-methylstyrene. Magnesium turnings (1.32 g) were placed in a two-necked flask fitted with a reflux condenser and dropping funnel, and a mixture of methyl iodide (12 g) and absolute ether (50 ml) was added from the funnel. When the magnesium had dissolved, a solution of 2',6'-dimethoxyacetophenone (11 g) in absolute ether (50 ml) was added (2',6'-dimethoxyacetophenone was prepared from 2',6'-dihydroxyacetophenone by the method described previously [1]; it boiled at 69-70°). When the whole of the solution of 2',6'-dimethoxyacetophenone had been added, the reaction mixture was set aside for 30 minutes, after which decomposition was effected by addition of ammonium chloride solution. The ether layer was separated in a separating funnel, washed several times with water, and dried with calcined sodium sulfate. The ether was distilled off, and the residue was vacuum-distilled. After three distillations 4.7 g (47.6%) was obtained of a substance of b.p. 136-138°/26 mm or 92-94°/3 mm.

2,6-Dimethoxy-α-methylstyrene was obtained in the form of clear crystals having an aromatic odor, m.p. 36-37°, d_4^{18} 1.043.

Found %: C 74.30, 74.55; H 8.16, 8.18.

$C_{11}H_{14}O_2$. Calculated %: C 74.13; H 7.92.

SUMMARY

1. An investigation has been made of the ability of 2,6-dimethoxy-α-methylstyrene and of 4-tert-butyl-α,2,6-trimethylstyrene to undergo polymerization, and it has been found that neither of these compounds is able to polymerize.

2. It has been suggested that the inability of 2,6-dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene to undergo polymerization is to be explained by stereochemical considerations, namely by the steric obstacles created by the α-methyl group and the two ortho-substituents.

3. It has been found that 4'-tert-butyl-2',6'-dimethylacetophenone does not react with organomagnesium compounds, but readily undergoes Shorygin's reaction with organosodium compounds.

4. 2,6-Dimethoxy-α-methylstyrene and 4-tert-butyl-α,2,6-trimethylstyrene have been synthesized.

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CHRONICLE

AT THE COMMITTEE FOR THE INVESTIGATION OF THE SCIENTIFIC HERITAGE OF D. I. MENDELEEV AND THE PUBLISHING OF HIS WORKS

In Leningrad on February 12th and 13th, 1953, there was a scientific session of the committee for the investigation of the scientific heritage of D. I. Mendeleev and the publishing of his works, which was held conjointly with the Leningrad section of the D. I. Mendeleev Chemical Society.

In his introductory address, Academician A. V. Topchiev remarked that in recent years a considerable number of D. I. Mendeleev's works and collections of papers throwing light on various aspects of the great Russian scientist's activities had been published, but it had to be acknowledged that we have not yet published an adequate number of his works and have not done enough toward their popularization. The position was particularly unsatisfactory with respect to the study of the D. I. Mendeleev archives and the publication of documents to be found there will form an important supplement to the published works of D. I. Mendeleev.

Academician A. V. Topchiev pointed out that, at the present time, the main problem of those investigating D. I. Mendeleev's works was the sorting out of his archives and the deciphering and study of the manuscripts. It was quite to be expected that all the reports read at these sessions of the committee would contain much new material found in the D. I. Mendeleev archives.

Now that all documents left after D. I. Mendeleev's death were concentrated in one place—the D. I. Mendeleev Archive-Museum at the A. A. Zhdanov University of Leningrad, the work of those investigating D. I. Mendeleev's works had been considerably lightened.

In an extensive report, "The Contribution of D. I. Mendeleev to Petroleum Science", Academician A. V. Topchiev drew a clear, vivid picture of the scientific, organizational, and technological activities of Mendeleev in the petroleum field. The large amount of archive material cited enabled a fuller picture of the actions and thoughts of the great Russian chemist to be obtained.

Already on his first acquaintance with the Baku petroleum establishments in 1863, Mendeleev made a number of suggestions that would permit an improvement in the technique of petroleum treatment, but his main attention, even at that time, turned to the necessity for the construction of petroleum pipelines. Archive material that has recently been found shows that in 1863 Mendeleev not only came to realize the necessity for the establishment of plants for the treatment of petroleum in the center of Russia, but also decided to take upon himself the technical direction of a plant which was to be constructed near Nizhny Novgorod. The various notes, plans, and texts of agreements with the petroleum industrialist V. A. Kokarev show the detailed manner in which D. I. worked out all the technological processes for the treatment of petroleum, into which he introduced many new features, and the great amount of attention he gave to the question of the transport of petroleum along the Volga, for which he proposed the use of tankers of his own design. All these documents characterize D. I. Mendeleev as a technologist.

Already in the first stages of his activities in the petroleum field, Mendeleev realized the enormous importance of scientific investigation. "Without science our work with petroleum will be in the dark", he said.

Academician Topchiev cited a large amount of archive material showing the extensive researches carried out by Mendeleev in the course of his studies of the composition of petroleums and their physical and chemical properties. The notebooks found in the Mendeleev Archives at Leningrad University have yielded some extremely important material, supplementary to D. I. 's published work on the investigation of petroleum. Thus, Mendeleev, using a pycnometer of his own design, determined with great accuracy the specific gravities of various petroleum fractions; also their coefficients of expansion. He carried out some investigations, very interesting both from the theoretical and the practical point of view, on the purification of petroleum products by the aid of chemical reagents; he examined the action on petroleum of various acids, ammonium chloride, and ammonia, and used as purifying agents fuller's earth, charcoal, pumice, and broken brick. In a study of the oxidation of petroleum products by atmospheric oxygen, Mendeleev showed that it was possible to separate the heavy fractions from petroleum by the action of selective solvents.

Academician A. V. Topchiev brought forward much material to show the steadfastness and inventiveness exhibited by Mendeleev in his efforts to achieve better fractionation of the petroleum by the aid of fractional distillation. Mendeleev constructed several pieces of apparatus in which he was able to separate the petroleum into two-degree fractions. Great interest was aroused by the photographs shown by Academician Topchiev of graphs from Mendeleev's notebooks, on these the ordinates were the mean boiling points of the fractions and the abscissae were their specific gravities. Mendeleev established that the specific gravity curve for petroleum is characterized by alternate minima and maxima, and he suggested on the basis of this fact that the petroleums studied contained at least two types of hydrocarbons, the lighter being saturated, and the heavier unsaturated. Academician Topchiev particularly emphasized that these conclusions, so important from the chemical point of view, were arrived at by Dmitry Ivanovich on the basis of purely physical and physicochemical methods of investigation. Now that he had exact methods for the characterization of petroleum at his command, D. I. Mendeleev was able to establish that the chemical composition of petroleum depends on the conditions of its geological occurrence.

Mendeleev persistently urged industrialists to improve their methods of treating petroleum, to use continuous methods of distillation, and to employ fractionation columns. While working in 1881 at the Konstantin works near to Yaroslavl, Mendeleev tried out new methods of distilling petroleum and a new, improved distillation plant, made to his design, under works conditions. Mendeleev was interested in the thermal treatment of petroleum--what was subsequently to be called "cracking".

Much interesting information was given by Academician Topchiev concerning the way D. I. Mendeleev strove for the full utilization of all of the substances found in petroleum. Mendeleev showed how extremely valuable petroleum is in the national economy and was the first to do so; and he was the first to proclaim, as he did in his papers and speeches, the necessity for the full processing and rational utilization of petroleum. At the beginning of the eighties, Mendeleev pointed out the possibility of obtaining aromatic hydrocarbons and organic dyes from petroleum. Owing to Mendeleev's persistence, valuable lubricating oils started to be produced in Russia, and kerosene (which was called photonaphthyl in the middle of the nineteenth century) was obtained in quantities that permitted not only the cessation of the importation of kerosene from America, but also its export to other countries. Mendeleev devoted much effort to the development of a method of preparing a safe illuminating oil, which he called bakuol. He took an active part in a competition for a safety lamp.

Only under the conditions of Soviet rule has Mendeleev's dream about petroleum come true. His desire that petroleum should be obtained in the island of Cheleken, in the north of Russia, and in the Povolzhy provinces has been fulfilled, and Mendeleev's prophetic words about petroleum as a raw material for the preparation of chemicals have come true.

In conclusion Academician A. V. Topchiev pointed out that the rich scientific heritage of D. I. Mendeleev in petroleum science and industry has not yet been developed to the extent that it should be. The numerous notebooks, record books, and separate notes by D. I. Mendeleev preserved in the scientific archives at the A. A. Zhdanov University of Leningrad conceal many ideas that can fertilize the creative thought of Soviet investigators. Careful study and development of the scientific heritage of D. I. Mendeleev will help Soviet petroleum scientists in their persistent every-day work on the study of the composition, properties, and treatment of petroleum with the object of solving the problem of the rational utilization of petroleum in accordance with the historic resolutions of the Nineteenth Congress of the Communist Party of the Soviet Union.

In connection with Academician Topchiev's report, the library of the USSR Academy of Sciences opened an exhibition entitled "D. I. Mendeleev and the Russian petroleum industry". The exhibition, which aroused great interest, consisted of six sections:

1. Information about petroleum in the Russian literature of the eighteenth century.
2. The petroleum industry in Russia before Mendeleev.
3. D. I. Mendeleev's work on petroleum.
4. The petroleum industry in Russia from Mendeleev to the Great October Socialist Revolution.
5. The petroleum industry in the Soviet Union.
6. Innovators in the petroleum industry.

Some of the staff of the Reference and Bibliographical Section of the library of the USSR Academy of Sciences--L. M. Gatkovi, N. N. Delkova, and O. P. Kamenogradskaya--organized the exhibition and were able to exhibit many little-known works.

A noteworthy exhibit in the first section was a copy of "Vedomosti" ("The News") issue no. 1 of 1703, in which there is a note entitled "News of the Presence of Petroleum in Kazan". Works by M. V. Lomonosov, F. P. Solmonov, I. Lepekhin, and other authors of the eighteenth century, which contain information concerning the occurrence of petroleum in Russia, were also worthy of note.

A particularly rich display of material was to be found in the section entitled "The petroleum industry in Russia from Mendeleev to the Great October Socialist Revolution". Here visitors to the exhibition saw the works of M. I. Konovalov, K. V. Kharichkov, V. V. Markovnikov, A. A. Letny, K. Lisenko, A. Kurbatov, and others.

The petroleum industry in the Soviet Union was represented by the works of the great Soviet academician-scientists—Gubkin, Zelinsky, Nametkin, Topchiev, and others—and also by numerous works by innovators in the petroleum industry.

Altogether, 160 books were exhibited.

The work of D. I. Mendeleev leading up to the discovery of the periodic law was the subject of an address by Prof. B. M. Kedrov. The speaker made an analysis of a number of recently discovered items by Mendeleev which show how the discovery of the great natural law came about. These items may be conveniently divided into three groups. The first group comprises documents of the earlier years of Mendeleev's scientific work (1856-1867)—from the time when he left the Chief Padagogical Institute to the date of his acceptance of the chair of chemistry in St. Petersburg University. These investigations include those on isomorphism, specific volumes, the theory of limits, etc., and they disclosed the relations between the elements which were later (1869) advanced in the form of physical and chemical functions of the atomic weights. Particular significance is to be attached to those items that indicate the way in which Mendeleev studied the problem of the determination of atomic weights and the distribution of elements into "natural groups".

The second group of items contains Mendeleev's notes in connection with his lectures at St. Petersburg University and with the composition of the first part of the "Principles of Chemistry" and the planning of the second part (from the end of 1867 to the beginning of 1869). This material led directly to the discovery of the periodic law, which occurred during work on the "Principles of Chemistry", as stated on several occasions by Mendeleev himself.

The third group of items comprises documents to which the date of the actual discovery—17th February 1869 (Old Style)—must be assigned. On that day Mendeleev had arranged to go out on a mission for the Free Economic Society, but he evidently did not go out, owing to his work on the first variants of the periodic system. Five documents are to be assigned to that day, and three of them, which are dated 17th February 1869, permit us to determine the moment of the beginning of the discovery and the moment of its completion during the course of that day, and also the course of this discovery as it became manifested in an ever fuller and deeper revelation of the relations between individual elements and whole groups of elements and in the embracing by the system of an ever increasing number of elements, until finally it embraced all of the 63 elements known at that time.

The newly discovered material enables us to determine many important details of the history of the great discovery made by Mendeleev. In particular, it confirms the supposition that, when discovering the periodic law, Mendeleev did not arrange the elements in one general series (according to their atomic weights) and then break this down into periods, but arranged them in groups in such a way that one group of elements was written below another in accordance with the atomic weights of their members.

B. M. Kedrov stated that all this material, and also Mendeleev's notes on his laboratory experimental investigations on chemistry carried out in 1869—1871, would be included in the second volume of the "Scientific Archives of D. I. Mendeleev", now in preparation; this, like the first volume of this series, is to be devoted to the periodic law.

In a report on "The Manuscripts of D. I. Mendeleev on the Theory of Limits", P. B. Dobrotin, a member of the staff of the Mendeleev Archives, gave some interesting information on Mendeleev's preparatory work on his theory of the limits of organic compounds. These manuscripts, now studied for the first time, belong to the year 1861, and in these can be seen, much more clearly than in the printed articles, the precursory thoughts and basic ideas leading Mendeleev to the finished theory of limits, which was expounded in special articles and in the book "Organic Chemistry".

The speaker considered that in his theory of limits Mendeleev expressed a view on chemical compounds that was very progressive at that time. D. I. Mendeleev, although not yet employing any scheme of valency distribution, clearly understood the possibility of learning the mutual influence of atoms in a molecule, thus completely refuting the theory of types. Simultaneously with the theory of limits, D. I. Mendeleev developed the concept of the forms of compounds. Both of these concepts (limits and forms) played a foremost part in the further work of D. I. Mendeleev and must be regarded as important stages on the road to the discovery of the periodic law.

The former personal secretary of the great Russian scientist, Alekseĭ Vasilyevich Skvortsov, shared with us some of his wide experience in the deciphering of Mendeleev's handwriting in the paper he gave entitled "Transcription of D. I. Mendeleev's manuscripts and their deciphering". Mendeleev's handwriting was distinguished by many peculiarities that make it not readily accessible to the reader. Thus, D. I., trying to put on paper the thoughts that came too fast for his pen, often abbreviated words and ran several words together.

A. V. Skvortsov showed by a number of examples the characteristic ways used by Mendeleev for the abbreviation of words and of combinations of groups of words. A great amount of practice is necessary in order to get used to these peculiarities in Mendeleev's writing. The speaker showed a large number of photographs of individual pages from the notebooks and diaries of Mendeleev and indicated how individual letters were written. The letters "Ys", "T", and "K" are particularly difficult to read; it is interesting that Mendeleev wrote the combination of the letters "c" and "t" as if it were the letter "b".

As a result of a great deal of hard work, A. V. Skvortsov has deciphered thirty-two notebooks, numerous working records, diary notes, jottings, letters, etc., comprising altogether about 2000 typewritten sheets.

Newcomers, now entering upon the study of the works of our great chemist, must acquire from A. V. Skvortsov the ability to decipher D. I. Mendeleev's manuscripts.

Members of the committee visited the D. I. Mendeleev Archive--Museum, where a session was held, under the chairmanship of Academician A. V. Topchiev, relating to various questions of organization and the publishing of material.

The space available for the museum has been considerably increased. The room that was for many years Mendeleev's study now forms part of the museum, and books and other objects that were actually in Mendeleev's study during his lifetime have now been placed there.

The staff of the museum now has the great task of staging an exhibition covering all aspects of the activities of the great Russian scientist.

TO THE MEMORY OF ACADEMICIAN NIKOLAI DMITRIEVICH ZELINSKY

The death occurred on July 31, 1953, at the age of ninety-two of the eminent chemist Academician Nikolai Dmitrievich Zelinsky, senior professor at the M.V. Lomonosov Moscow State University, Hero of Socialist Labor, recipient of three Stalin prizes, and holder of four Orders of Lenin and two orders of the Red Banner of Labor. In the person of Zelinsky Soviet science has lost a great organic chemist, founder of the science of heterogeneous organic catalysis and of petroleum chemistry, inventor of the first universal charcoal gas mask in the world, scientist of manifold activities, and teacher and trainer of several generations of chemists.

Zelinsky was the author of about six hundred original scientific papers and inventions in the fields of organic, physical, and inorganic chemistry, including petroleum chemistry and the chemistry of artificial liquid fuel. The investigations of Zelinsky and his school, the largest in the USSR on the synthesis of hydrocarbons, organic catalysis, petroleum chemistry, and protein chemistry, have occupied and continue to occupy a leading position in world science.

N. D. Zelinsky was born on February 6 (New Style), 1861, in Tiraspol in the province of Kherson (now Moldavian Autonomous SSR). At the age of two he lost his father, and a year and a half later his mother died also. He was brought up by his maternal grandmother, M. P. Vasilyeva, a good, sympathetic, cultured woman, very progressive in ideas for the time in which she lived; Zelinsky retained fond memories of her to the last days of his life. He received his early education from his grandmother, and she provided for his further education at the Richelyevsky Gymnasium in Odessa, which he attended until 1880. While still a schoolboy, Zelinsky listened enthusiastically to the lectures of the eminent physiologist I. M. Sechenov at the university. From the gymnasium, Zelinsky passed to the Natural History Department of the Physico-mathematical Faculty of the Novorossiisky University (Odessa), which he attended until 1884. His first chemistry teachers at the university were F. F. Klimenko, A. A. Verigo, V. M. Petriev, and P. G. Melikov (Melikishvili). It was under the direction of Melikov that Zelinsky, as a student, carried out his first scientific investigation on the "Product of the Addition to Methylamine to β-Methylglycidic Acid", which was published in 1884 in the Journal of the Russian Physicochemical Society.

With regard to his first teacher, P. G. Melikov, Zelinsky wrote with great warmth of feeling in 1950: "All my life I have been constantly grateful to my teacher for the attention and cooperation that he gave to me over a period of many years"; and also "The memory of this man, who was my first teacher, I preserve as the best of my memories of my student days at the Novorossiisky University".

In biology Zelinsky's teachers included the eminent Russian scientists A. O. Kovalevsky (zoology), I. I. Mechnikov (embriology and evolutionary theory), and L. S. Tsenkovsky (botany).

Personal intercourse and friendship with his eminent teachers, and later with the giants of Russian progressive science — I. M. Sechenov, K. A. Timiryazev, P. N. Lebedev, N. A. Umov, and A. G. Stoletov — had an exceptional, favorable influence on the formation of the materialistic world-view of N. D. Zelinsky, whose interests in the future were to range over such a wide field of science, and who as a research chemist was to enter into the highest ranks of the creators of world chemical science.

Soon after completing his course at the Novorossiisky University, Zelinsky was sent as a faculty stipendiary to Germany, where he worked under the great organic chemists of that time, J. Wislicenus (Leipzig) and Prof. Victor Meyer (Göttingen), and then somewhat later, during his second visit abroad, under the famous Wilhelm Ostwald, one of the founders, after Lomonosov, of classical physical chemistry.

The investigational work carried out by the young Zelinsky under the direction of these great chemists determined, to a great extent, the three important directions of his subsequent investigations. He began some